

GREAT LAKES  
DREDGED MATERIAL TESTING AND EVALUATION MANUAL

APPENDIX F  
METHODS FOR CHEMICAL AND PHYSICAL ANALYSES

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## BACKGROUND ON PARAMETER AND METHOD SELECTION

### Purpose

This appendix contains detailed methods for the physical and chemical analysis of sediments, water and elutriates to be used as part of the testing and evaluation of dredged material. The USEPA/USACE Task Group which developed the Great Lakes Dredged Material Testing and Evaluation Manual determined to have such detailed methods provided in this appendix for several reasons, including:

- identify analytical methods capable of meeting data quality objectives for dredged material testing,
- provide more uniformity and comparability of results between projects and laboratories, and
- enable districts and permit applicants to use methods as part of requirements in laboratory contracts.

The methods provided in this appendix should be capable of meeting the data quality objectives of the majority of dredged material testing projects in the Great Lakes. Alternate analytical methods may be considered for use in dredged material evaluations following the procedures described in Appendix E, Quality Assurance Guidance.

### Parameter Selection

To provide guidance on Tier 2 evaluations, the USEPA/USACE Task Group developed a generic list of contaminants of concern. This list (table 1 in main text) is not intended to be all inclusive, but was developed as a "starting place" for project-specific evaluations. These contaminants were selected based on ecological or toxicological significance and their recorded presence in many Great Lake harbors and tributaries. In addition to the chemical parameters on this list, methods were selected for other physical and chemical parameters for the following reasons:

- the parameter was a reliable indicator of the presence of other contaminants (i.e., volatile solids and TPH), and
- the parameter was needed for use in TBP analysis or the STFATE mixing model (i.e., TOC, density, and grain size).

Additionally, the Task Group had to determine for which matrices (e.g., sediments, water/elutriate, or both) the methods would be prepared. The final list of selected parameters contained 22 parameters to be analyzed in sediments, water/elutriate, or both matrices (Table F-1). A method for the preparation of elutriates from sediment samples has also been included.

Table F-1. Parameters for Methods Selection

<u>Parameter</u>	<u>Matrix<sup>a</sup></u>
Total Solids	S
Total Volatile Solids	S,E
Total Dissolved Solids	E
Total Suspended Solids	E
Specific Gravity	S
Grain Size	S
Ammonia	S,E
Cyanide	S,E
As	S,E
Cd	S,E
Cr	S,E
Cu	S,E
Hg	S,E
Ni	S,E
Pb	S,E
Zn	S,E
Total Organic Carbon	S
Chloro-Pesticides	S,E
Total PCBs	S,E
Total Petroleum Hydrocarbons	S,E
Phenolics	S,E
Polynuclear Aromatic Hydrocarbons	S,E

<sup>a</sup> S = sediment; E = water and elutriate.

It should be noted that evaluators need to develop a site-specific contaminants of concern list for each dredging project which may contain all, some part, or other parameters not identified in the methods manual appendix. It is the intention of the USEPA and USACE to prepare descriptions of additional physical and chemical analytical methods for sediments, water, elutriate, and animal tissues in future amendments to the Great Lakes Dredged Material Testing and Evaluation Manual.

#### Base Method Selection

The selection of appropriate published methods to be used as base methods for each parameter was also performed by committee. A new committee was selected of scientists from the USACE North Central Division; USACE Districts in Chicago, Detroit, and St. Paul; USACE Waterways Experiment Station; USEPA Regions 2, 3, and 5; USEPA Great Lakes National Program Office; USEPA Environmental Monitoring and Systems Laboratory - Las Vegas; and Lockheed Environmental Systems & Technologies Company.

To each member of the methods committee, a questionnaire was sent requesting a list of the most commonly used methods for each parameter in their laboratory, district, or Region. This list of commonly used methodologies was compiled and conference calls were held every other week to discuss and come to agreement on a common base method. After selection of the base method for each parameter, a final conference call was held to select an appropriate format for the methods presentation. For each parameter presented in this appendix, the method has been prepared in the agreed upon format by the methods committee and the base method has been referenced in the Scope and Application section (section 1.).

# TOTAL SOLIDS

## 1.0 Scope and Application

This method is applicable to the determination of total solids in sediment samples.

The results of this analysis are used in the analytical laboratory to convert all results in which field-moist samples are used to oven-dry weight basis. Additionally, the end product or residue created from this procedure can be used in the determination of total volatile solids (TVS).

Since this method is based on the difference between two weighings, the range and sensitivity of the method is dependent upon the balance used.

This method is based on EPA Method 160.3 (USEPA, 1983).

## 2.0 Summary of Method

A well mixed aliquot of sediment is quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness at 103-105° C. Total solids is determined by expressing the sample weight loss as a percentage of the original field moist sample weight.

## 3.0 Interferences

Non-representative particulates, such as leaves, sticks, fish, and lumps of fecal matter, should be excluded from the sample if it is determined that their inclusion is not desired in the final result.

Residues dried at 103-105° C may retain not only water of crystallization but also some mechanically occluded water. Because removal of occluded water is marginal at this temperature, attainment of constant weight may be very slow (APHA, 1989).

Loss of CO<sub>2</sub> will result in conversion of bicarbonate to carbonate. Loss of organic matter by volatilization will usually be slight (APHA, 1989).

Results for samples high in oil and grease may be questionable because of the difficulty of drying to a constant weight in a reasonable time (APHA, 1989).

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Oven.
4. Thermometer, 0 to 200° C range, graduated to 1° C.
5. Desiccator and desiccant. Desiccants generally used include: anhydrous calcium sulfate, silica gel, or phosphorus pentoxide. Indicating desiccants are preferable since they show when the desiccant needs to be changed or regenerated.

### 4.2 Materials

1. Evaporating dishes, porcelain, 90 mm, 100 ml capacity. (Aluminum, Vycor, or platinum weighing dishes may be substituted and smaller size dishes may be used, if required.)

## 5.0 Reagents and Standards

No reagents are required for this procedure.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Since field-moist samples are used in the determination, preservation of the sample is not practical. Therefore, analysis should begin as soon as possible after sample collection to minimize loss of sample moisture prior to analysis. A holding time of 7 days is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C) to minimize microbiological decomposition of solids between sample collection and sample analysis.

All sample containers must be prewashed with detergents. If samples are to be analyzed for other parameters, acids and Type II water washings may also be required. Either glass or plastic containers can be used for the storage of samples to be analyzed for total solids.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^{\circ}$  C.

The oven should be monitored to ensure that temperature fluctuation does not exceed  $\pm 2^{\circ}$  C.

## 8.0 Procedure

1. Heat the clean evaporating dish to 103-105° C for one hour prior to the determination of total solids of the sample. If TVS is also to be determined on the sample, the evaporating dish should be heated at  $550 \pm 50^{\circ}$  C for one hour in a muffle furnace prior to use. Cool in a desiccator, weigh, and store in desiccator until ready for use.
2. Allow oven to equilibrate at 103 to 105° C overnight.
3. Tare each weighing dish to the nearest 0.01 g and record the weight.
4. Transfer 25 g of the homogenized, field-moist sediment sample into the pre-weighed dish. Weigh the dish + moist sample to the nearest 0.01 g and record the weight.
5. Place the sample in the oven and evaporate to dryness.
6. Dry the evaporated sample for at least 1 hour at 103-105° C. It is recommended that during the initial drying step, the samples be left in the oven for 2 to 3 hours.
7. Remove weighing pan from oven. Allow sample to cool in a desiccator for at least 1 hour. Weigh each sample to 0.01 g.

8. Repeat the cycle of drying at 103-105° C, cooling in a desiccator, weighing, and recording the weight until a constant weight is obtained or until observed weight loss on drying is less than 5% of the previous weight, or 0.5 mg, whichever is less.

**NOTE:** Alternately, the sample may be placed in the oven and dried at 103-105° C overnight and cooled in a desiccator. No differences in sample color, indicating moisture, should be noticeable upon visual examination of the sample. If differences are identified, continue drying the sample following the procedure in step 8.

9. Weigh the sample dish to the nearest 0.01 g and record final weight of the sample + dish.

## 9.0 Quality Control

### 9.1 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 10 percent or less.

### 9.2 Blanks

A minimum of one blank per sample batch should be analyzed. A blank for total solids consists of an empty dish. The weight change of the blank should not be greater than  $\pm 0.5$  mg.

## 10.0 Method Performance

In a study involving four sets of 10 determinations by two analysts, the method produced results with a calculated standard deviation of 5.2 mg/L at 15 mg/L, 24 mg/L at 242 mg/L, and 13 mg/L at 1707 mg/L. These results were derived with waste water samples rather than sediment samples (APHA, 1989) but indicate the precision that can be attained with this method.

## 11.0 Calculations and Reporting

Use the results of the individual weighings to calculate total solids as follows:

$$\text{Total Solids, \%} = \frac{(A - B) \times 100}{(A - D)}$$

where:

A = weight of moist sample + dish, g

B = weight of dried sample + dish, g

D = weight of evaporating dish, g

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. 17th Edition, APHA, New York, New York. p. 2-71 - 2-79.

U.S. Environmental Protection Agency. 1983. Methods for the Chemical Analysis of Water and Wastes. EPA-600/4-79-020. U.S. Environmental Protection Agency, Environmental Monitoring and Systems Laboratory, Cincinnati, Ohio.

# TOTAL VOLATILE SOLIDS IN SEDIMENTS

## 1.0 Scope and Application

This method determines the weight of material associated with a sediment sample that is volatile or combustible at 550° C. The test is useful in obtaining a rough approximation of the amount of organic matter present in the solid fraction of bottom sediments.

The sediment used for the determination of total volatile solids may be obtained from the original sample or from the residue obtained in the determination of total solids.

**NOTE:** If the aliquot is obtained from the original sample, then the procedure for total solids must be performed on the aliquot prior to ashing in the muffle furnace.

Since this method is based on the difference between two weighings, the range and sensitivity of the method is dependent upon the balance used.

This method is based on EPA Method 160.4 (USEPA, 1983).

## 2.0 Summary of Method

The residue obtained after the determination of total solids is ignited at 550° C in a muffle furnace. The loss of weight on ignition is reported as mg/kg or weight percent (%) of total volatile solids.

## 3.0 Interferences

Since the procedure is operationally defined and based on the difference between two weighings, the test is subject to errors due to loss of water of crystallization, loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics, and decomposition of mineral salts during combustion.

The principal source of error in the determination is failure to obtain a representative sample.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.001 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Muffle furnace.
4. Thermocouple, 0 to 600° C range, graduated to 1° C.
5. Desiccator and desiccant. Desiccants generally used include: anhydrous calcium sulfate, silica gel, or phosphorus pentoxide. Indicating desiccants are preferable since they show when the desiccant needs to be changed or regenerated.

### 4.2 Materials

1. Evaporating dishes or crucibles, porcelain, 90 mm, 100 mL capacity. (Aluminum, Vycor, or platinum weighing dishes or crucibles may be substituted and smaller size dishes may be used, if required.)

## 5.0 Reagents and Standards

No reagents are required for this procedure.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Since field-moist samples are used in the determination, preservation of the sample is not practical. Therefore, analysis should begin as soon as possible after sample collection to minimize loss of sample moisture prior to analysis. A holding time of 7 days is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C) to minimize microbiological decomposition of solids between sample collection and sample analysis.

All sample containers must be prewashed with detergents. If samples are to be analyzed for other parameters, acids and Type II water washings may also be required. Either glass or plastic containers can be used for the storage of samples to be analyzed for total volatile solids.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The oven should be monitored to ensure that temperature fluctuation does not exceed  $\pm 2^{\circ}$  C.

## 8.0 Procedure

1. Heat muffle furnace to  $550 \pm 10^{\circ}$  C.
2. Ignite residue produced from the determination of total solids at  $550 \pm 10^{\circ}$  C to ash the sample overnight in a muffle furnace.
3. Remove the sample dish from the furnace and allow to partially cool until most of the heat has been dissipated (about 15 minutes).
4. Transfer the sample to a desiccator for final cooling.
5. Weigh sample dish to the nearest 0.01 g and record final weight of the sample + dish.

## 9.0 Quality Control

### 9.1 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 10 percent or less.

## 9.2 Blanks

A minimum of one blank per sample batch should be analyzed. A blank for total volatile solids consists of an empty dish. The weight change of the blank should not be greater than  $\pm 0.5$  mg.

## 10.0 Method Performance

A collaborative study involving three laboratories examining four samples by means of ten replicates produced a standard deviation of  $\pm 11$  mg/L at a volatile residue concentration of 170 mg/L (APHA, 1989; USEPA, 1983).

## 11.0 Calculations and Reporting

Use the results from the individual weighings to calculate the total volatile solid content of the sample as follows:

$$\text{Total Residue, \%} = \frac{(A - B) \times 100}{(A - C)}$$

where:

A = weight of dried residue plus dish before ignition, g.

B = weight of the ashed sample plus dish, g.

C = original weight of dish, g.

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. 17th Edition, APHA, New York, New York. p. 2-71 - 2-79.

U.S. Environmental Protection Agency. 1983. "Methods for the Chemical Analysis of Water and Wastes". EPA-600/4-79-020. U.S. Environmental Protection Agency Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. March.

# SPECIFIC GRAVITY

## 1.0 Scope and Application

This method is applicable to the determination of specific gravity of sediment samples. Unless otherwise required, specific gravity values will be based on water at 20° C.

The specific gravity of a sample for use in sediments engineering calculations is usually expressed in three different forms:

1. specific gravity of solids,  $G_s$ ,
2. apparent specific gravity,  $G_a$ , and
3. bulk specific gravity,  $G_m$ .

The specific gravity of solids is applied to samples with a particle size that will pass through a No. 4 sieve (particles with mean diameters less than 4.76 mm or 0.187 in). The specific gravity of solids is not applied to coarse particles because they normally contain voids from which air cannot be displaced unless the samples are pretreated by grinding to reduce particle size and eliminate the voids. In contrast, the apparent and bulk specific gravities are applied to samples with particle sizes that will not pass through a No. 4 sieve. Thus, when dealing with coarser particles, it is more convenient to work with the apparent specific gravity of the particle mass.

The values of  $G_s$  or  $G_a$  are used in all calculations involving fundamental properties of a sediment mass. The bulk specific gravity is used in special calculations, such as corrections of density and water content, for sediments containing gravels.

This method is based on a procedure in Appendix IV of the Corps of Engineers engineering manual (1970).

## 2.0 Method Summary

An aliquot of sediment is weighed to determine its mass. The sample is then transferred to a volumetric flask to determine the volume of distilled water that would be displaced by the tared aliquot. The ratio of weight of sediment sample in air to the weight of displaced water is the specific gravity of the sample.

The types of specific gravity determinations that can be completed with this method include the following:

1. **Specific Gravity of Solids.** The specific gravity of a sediment sample,  $G_s$ , is the ratio of the weight in air of a given volume of sediment particles at a stated temperature to the weight in air of an equal volume of distilled water at the same stated temperature.
2. **Apparent Specific Gravity.** The apparent specific gravity of a sediment sample,  $G_a$ , is the ratio of the weight in air of a given volume of the impermeable portion of a permeable material (that is, the solid matter including its impermeable pores or voids) at a stated temperature to the weight in air of an equal volume of distilled water at the same stated temperature.
3. **Bulk Specific Gravity.** The bulk specific gravity of a sediment sample,  $G_m$ , is the ratio of the weight in air of a given volume of a permeable material (including both permeable and impermeable voids normal to the material) at a stated temperature to the weight in air of an equal volume of distilled water at the same stated temperature.

### 3.0 Interferences

Potential errors associated with specific gravity measurements include the following:

1. **Imprecise weighing of flask and contents.** Since the computation of the specific gravity of solids is based on a difference in weights which is small in comparison with the weights themselves, the same balance should be used for calibrating the volumetric flask and for determining the specific gravity whenever the calibration curve is used.
2. **Temperature of flask and contents not uniform.** Both in calibrating the flask and determining the specific gravity, utmost care should be taken to insure that measured temperatures are representative of the flask and contents during the times when the weighings are made.

3. Flask not clean. The calibration curve will not remain valid if accumulation of residue changes the tared weight of the flask. Also, if the inside of the neck is not clean, an irregular meniscus may form.
4. Moisture on outside of flask or inside of neck. When calibrating the flask for a temperature lower than room temperature, there is a tendency for condensation to form on the flask despite careful drying and rapid weighing. Whenever possible, weighing should be done at approximately the same temperature as that of the flask.
5. Meniscus not coincident with mark on neck of flask. One drop of water too much makes an error of approximately 0.05 g. This error can be minimized by taking the average of several readings at the same temperature. When the suspension is opaque, a strong light behind the neck is helpful in seeing the bottom of the meniscus.
6. Use of water containing dissolved solids. It is essential that ASTM Type I water be used exclusively to insure the continued validity of the flask calibration curve.
7. Incomplete removal of entrapped air from sample suspension. This is the most serious source of error in the specific gravity determination and will tend to lower the computed specific gravity. The suspension must be thoroughly evacuated or boiled and the absence of entrapped air verified as described in the note of step 5 in section 8.1.1. (It should be noted that air dissolved in the water will not affect the results, so it is not necessary to apply vacuum to the flask when calibrating or after filling the flask to the calibration mark.)
8. Gain in moisture of oven-dried specimen before weighing. If the specimen is oven-dried before the specific gravity determination, it must be protected against a gain in moisture until it can be weighed and placed in the flask.
9. Loss of material from oven-dried specimen. If the specimen is oven-dried and weighed before being placed in the flask, any loss of material will lower the computed specific gravity.

Potential errors associated with apparent and bulk specific gravity measurements include the following:

1. Loss of moisture from saturated surface-dry particles before weighing. Unless the saturated surface-dry material is weighed

promptly, evaporation may cause an increase in the computed bulk specific gravity.

2. Failure to correct for the change in density of water with temperature. This correction is often overlooked when computing either the apparent or bulk specific gravity.

## 4.0 Apparatus and Materials

### 4.1 Specific Gravity Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Volumetric flask, 500 mL capacity.
4. Vacuum pump with vacuum gauge, piping and tubing for connections to each flask. The connection to each flask should include a trap to catch any water drawn from the flask.
5. Oven.
6. Thermometer, range 0 to 50° C, graduated in 0.1° degree
7. Evaporating dish, glass or porcelain, capable of holding 600 mL.
8. Water bath.
9. Sieve, U. S. Standard No. 4 conforming to ASTM Designation: E11, Standard Specifications for Sieves for Testing.

### 4.2 Apparent and Bulk Specific Gravity Apparatus

1. Balance, having capacity of 5 kg or more and sensitive to 1.0 g.
2. Wire basket of No. 6 mesh, approximately 20 cm in diameter and 20 cm high.
3. Suitable container for immersing the wire basket in water, and suitable apparatus for suspending the wire basket from the center of the balance scale pan.
4. Thermometer, range 0 to 50° C, graduated in 0.1° degree.

## 5.0 Reagents and Standards

1. ASTM Type I water (ASTM, 1984).

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Some samples, particularly those with a high organic content, are sometimes difficult to rewet after having been oven-dried. Therefore, it is recommended that samples be stored in their field-moist state until used in the procedure.

Samples should be stored at 4° C between sample collection and analysis.

All sample containers must be prewashed with detergents. If samples are to be analyzed for other parameters, acids and Type II water washings may also be required. Either glass or plastic containers can be used for the storage of samples to be analyzed for specific gravity.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^\circ \text{C}$ .

The oven and water bath temperatures should be monitored to ensure that temperature fluctuation does not exceed  $\pm 2^\circ \text{C}$ .

The volumetric flask shall be calibrated for the weight of the flask and water at various temperatures. The flask and water are calibrated by direct weighing at the range of temperatures likely to be encountered in the laboratory. The calibration procedure is as follows:

1. Fill the flask with deaired water to slightly below the calibration mark and place in a water bath at a temperature between 30 and 35° C. Allow the flask to remain in the bath until the water in the flask reaches the temperature of the water bath. This may take several hours.
2. Remove the flask from the water bath and adjust the water level in the flask so that the bottom of the meniscus is even with the calibration mark on the neck of the flask.
3. Thoroughly dry the outside of the flask and remove any water adhering to the inside of the neck above the graduation
4. Weigh the flask and water to the nearest 0.01 g. Immediately after weighing, shake the flask gently and determine the temperature of the water to the nearest 0.1° C by immersing a thermometer to the mid-depth of the flask.
5. Repeat the procedure outlined in step 1 at approximately the same temperature. Make two additional determinations, one at room temperature and the other at approximately 5 degrees cooler than room temperature.
6. Draw a calibration curve showing the relation between temperature and corresponding weight of the flask + water.
7. Prepare a calibration curve for each flask used for specific gravity determined and maintain the curves as a permanent record.

## 8.0 Procedure

### 8.1 Specific Gravity Procedure

Prior to the determination of specific gravity, the sample to be tested should be sieved on a No. 4 sieve. That portion of the sample that passes the No. 4 sieve is used for the specific gravity determination and that portion of the sample retained by the No. 4 sieve is used for the apparent and bulk specific g gravity determination.

If the samples are sieved in a field-moist state, proceed as directed in section 8.1.1. If the samples are air-dried prior to being sieved, proceed as directed in paragraph 8.1.2.

### 8.1.1 Procedure for Field-Moist Samples.

1. Select a representative sample aliquot of the sieved sample passing a No. 4 sieve, ranging between 50 g (for cohesive sediments) and 150 g (for cohesionless sediments) and weigh the sample to the nearest 0.01 g in a dish or beaker.
2. Add 50 to 100 mL water to the sample and mix with a spatula to form a slurry.
3. Transfer the sample slurry to a calibrated volumetric flask and fill the flask approximately half full with water.
4. Connect the flask to the vacuum line and apply a vacuum of approximately 73.5 cm (29 in) mercury. Agitate the flask gently at intervals during the evacuation process.

**NOTE:** The length of time that vacuum should be applied will depend on the properties of the sample being tested. Samples with a high plasticity or high organic content may require 6 to 8 hr and other samples may require considerably less time for removal of entrapped air.

**NOTE:** To ensure continuous boiling, the temperature of the flask and contents may be elevated somewhat above room temperature by immersing in a water bath at approximately 35° C. Alternatively, entrapped air may be removed by boiling (see following note). Allow flask and contents to cool, preferably overnight, before filling and checking in step 5.

**NOTE:** Air removal from organic sediments usually cannot be accomplished by the application of vacuum. In this case it will be necessary to boil the suspension contained in the flask for about 30 min, adding distilled or demineralized water carefully from time to time to prevent boiling the sample dry. The flask should at all times be approximately half full.

5. Fill the flask with deaired water to about 2 cm below the 500 mL graduation and apply a vacuum slightly less than that which will cause vigorous boiling in order to prevent loss of sample.

**NOTE:** To determine if the suspension is deaired, slowly release the vacuum and observe the lowering of the water surface in the neck of the flask. If the water surface is lowered

less than 0.3 cm, the suspension can be considered sufficiently deaired. If the water surface is lowered more than 0.3 cm, Step 4 should be repeated.

6. Fill the flask until the bottom of the meniscus is coincident with the calibration line on the neck of the flask.
7. Thoroughly dry the outside of the flask and remove the moisture on the inside of the neck by wiping with a paper towel. Weigh the flask and contents to the nearest 0.01 g. Immediately after weighing, stir the suspension to assure uniform temperature, and determine the temperature of the suspension to the nearest 0.1° C by immersing a thermometer to the mid-depth of the flask.
8. Record the weight of the flask containing the sample suspension and the temperature of the sample.
9. Carefully transfer the contents of the flask to an evaporating dish.
10. Rinse the flask with distilled water to ensure removal of all of the sample from the flask.
11. Oven dry the sample to a constant weight at a temperature of 103-105° C. Allow the residue to cool to room temperature in a desiccator and determine the weight of the sample to the nearest 0.01 g.
12. Record all weights.

#### 8.1.2 Procedure for Air-Dried Samples

1. Oven dry that portion of the sieved sample passing a No. 4 sieve at 103-105° C and cool to room temperature in a desiccator.
2. Select a sample aliquot ranging between 50 g (for cohesive sediments) and 150 g (for cohesionless sediments) and weigh the sample to the nearest 0.01 g. Quantitatively transfer the sediment to a volumetric flask, taking care not to lose any material during this operation.

**NOTE:** To avoid possible loss of preweighed sediment, the sample may be weighed after transfer to the flask.

3. Fill the flask approximately half full with deaired distilled water and allow the suspension to stand overnight.

4. Connect the flask to the vacuum line and apply a vacuum of approximately 73.5 cm (29 in) mercury for approximately 2 to 4 hr.

**NOTE:** Entrapped air may also be removed by boiling as previously discussed. However, the process should be observed closely to avoid loss of material during boiling. Allow flask and contents to cool, preferably overnight, before filling and checking.

5. Fill the flask with deaired distilled water to about 2 cm below the 500 mL graduation and apply a vacuum slightly less than that which will cause vigorous boiling in order to prevent loss of sample.

**NOTE:** To determine if the suspension is deaired, slowly release the vacuum and observe the lowering of the water surface in the neck of the flask. If the water surface is lowered less than 0.3 cm, the suspension can be considered sufficiently deaired. If the water surface is lowered more than 0.3 cm, Step 4 should be repeated.

6. Fill the flask until the bottom of the meniscus is coincident with the calibration line on the neck of the flask.
7. Thoroughly dry the outside of the flask and remove the moisture on the inside of the neck by wiping with a paper towel. Weigh the flask and contents to the nearest 0.01 g. Immediately after weighing, stir the suspension to assure uniform temperature, and determine the temperature of the suspension to the nearest 0.1° C by immersing a thermometer to the mid-depth of the flask.
8. Record the weight of the flask containing the sample suspension and the temperature of the sample.
9. Record all weights.

## 8.2 Apparent Specific Gravity and Bulk Specific Gravity

1. Wash the sample material retained on a No. 4 sieve thoroughly with water to remove dust or other coatings from the surface of the sample.
2. Immerse the sample material in water at 15 to 25° C for a period of 24 hr.

3. Remove the sample material from the water and roll it in a large absorbent cloth or tissue until all visible films of water are removed, although the surfaces of the particles may still appear to be damp. Wipe large particles individually.

**NOTE:** Take care to avoid excess evaporation during the operation of surface drying.

4. Transfer the sample to a tared beaker or weighing dish to obtain the weight of the saturated, surface-dry material. These results, and those of all subsequent weighings, should be reported to the nearest 1.0 g.
5. Immediately after weighing, place the sample in the wire basket and determine the weight of the sample in water. Measure and record the temperature of the water in which the specimen is immersed to the nearest 0.1° C.
6. Remove the sample from the wire basket and transfer to a beaker. Oven-dry the sample to a constant weight at a temperature of 103-105° C. After cooling to room temperature, weigh the sample.
7. Record all weights.

## 9.0 Quality Control

### 9.1 Replicates

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 10 percent or less.

## 10.0 Method Performance

None identified.

## 11.0 Calculations

### 11.1 Specific Gravity

The specific gravity of the sample is calculated to two decimal places using the following formula:

$$G_s = \frac{W_s \times K}{W_s + W_{bw} - W_{bws}}$$

where:

$G_s$  = the specific gravity of the sample, g/cm<sup>3</sup>

$W_s$  = the dry weight of the sample, g

$K$  = correction factor based on the density of water at 20° C from Table 1. Unless otherwise required, specific gravity values should be based on water at 20° C.

$W_{bw}$  = weight of flask plus water at test temperature, g (obtained from calibration curve)

$W_{bws}$  = weight of flask plus water plus wet sample at test temperature, g.

## 11.2 Apparent Specific Gravity

The apparent specific gravity of the sample is calculated to two decimal places using the following formula:

$$G_a = \frac{A \times K}{A - C}$$

where:

$G_a$  = the apparent specific gravity of the sample, g/cm<sup>3</sup>

$A$  = weight of dry sample, g

$K$  = correction factor based on the density of water at 20° C from Table 1

$C$  = weight of saturated sample suspended in water, g

## 11.3 Bulk Specific Gravity

The bulk specific gravity of the sample is calculated to two decimal places using the following formula:

$$G_m = \frac{A * K}{B - C}$$

where:

$G_m$  = the bulk specific gravity of the sample, g/cm<sup>3</sup>

A = weight of dry sample, g

K = correction factor based on the density of water at 20° C from Table 1

B = weight of saturated, surface dry sample, g.

C = weight of saturated sample suspended in water, g.

#### 11.4 Combined Fraction Specific Gravity

When a sample is composed of particles both larger and smaller than the openings of a No. 4 sieve, the specific gravity of the sample for use in engineering calculations should be computed as follows:

$$G = 100 \left[ \frac{(\% \text{ passing No. 4 sieve})}{G_s} + \frac{(\% \text{ retained on No. 4 sieve})}{G_a} \right]$$

where all terms are as defined above.

#### 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. Army Corps of Engineers. 1970. Specific Gravity. *In* Engineering Manual, Laboratory Soils Testing. EM 1110-2-1906. Compiled by Headquarters, Department of the Army, Office of the Chief Engineer. Updated by Change 1, May 1, 1980 and Change 2, August 29, 1986.

Table 1. Relative Density of Water and Correction Factor (K) for Various Temperatures<sup>1</sup>.

Temp °C	Relative Density	Correction Factor, K <sup>2</sup>	Temp °C	Relative Density	Correction Factor, K	Temp °C	Relative Density	Correction Factor, K
18.0	0.99862	1.0004	23.0	0.99756	0.9993	28.0	0.99626	0.9980
.1	60	4	.1	54	3	.1	23	0
.2	58	4	.2	51	3	.2	20	0
.3	56	3	.3	49	3	.3	17	0
.4	54	3	.4	46	2	.4	14	79
.5	52	3	.5	44	2	.5	11	9
.6	50	3	.6	42	2	.6	08	9
.7	49	3	.7	39	2	.7	06	8
.8	47	2	.8	37	1	.8	03	8
.9	45	2	.9	34	1	.9	00	8
19.0	0.99843	1.0002	24.0	0.99732	0.9991	29.0	0.99597	0.9977
.1	41	2	.1	29	1	.1	94	7
.2	39	2	.2	27	0	.2	91	7
.3	37	1	.3	24	0	.3	88	6
.4	35	1	.4	22	0	.4	85	6
.5	33	1	.5	20	0	.5	82	6
.6	31	1	.6	17	89	.6	79	6
.7	29	1	.7	14	9	.7	76	5
.8	27	0	.8	12	9	.8	73	5
.9	25	0	.9	09	9	.9	70	5
20.0	0.99823	1.0000	25.0	0.99707	0.9988	30.0	0.99567	0.9974
.1	21	0	.1	04	8	.1	64	4
.2	19	0	.2	02	8	.2	61	4
.3	17	0.9999	.3	699	8	.3	58	3
.4	15	9	.4	97	7	.4	55	3
.5	13	9	.5	94	7	.5	52	3
.6	10	9	.6	91	7	.6	49	3
.7	08	8	.7	89	7	.7	46	2
.8	06	8	.8	87	6	.8	43	2
.9	04	8	.9	84	6	.9	40	2
21.0	0.99802	0.9998	26.0	0.99681	0.9986	31.0	0.99537	0.9971
.1	00	8	.1	78	6	.1	33	1
.2	798	8	.2	76	5	.2	30	1
.3	96	7	.3	73	5	.3	27	0
.4	93	7	.4	70	5	.4	24	0
.5	91	7	.5	68	4	.5	21	0
.6	89	7	.6	65	4	.6	18	69
.7	87	6	.7	63	4	.7	15	9
.8	85	6	.8	60	4	.8	12	9
.9	83	6	.9	57	3	.9	09	9
22.0	0.99780	0.9996	27.0	0.99654	0.9983	32.0	0.99505	0.9968
.1	78	6	.1	51	3	.1	02	8
.2	75	5	.2	48	2	.2	499	8
.3	73	5	.3	46	2	.3	96	7
.4	70	5	.4	43	2	.4	93	7
.5	68	5	.5	40	2	.5	90	7
.6	65	4	.6	37	1	.6	86	6
.7	63	4	.7	34	1	.7	83	6
.8	61	4	.8	32	1	.8	80	6
.9	58	4	.9	29	1	.9	77	5

<sup>1</sup> - Relative density of water based on density of water at 4° C equal to unity. The values given are numerically equal to the absolute density in grams/milliliter (for sediment testing purposes, g/mL = g/cm<sup>3</sup>). Data obtained from Smithsonian Tables, compiled by various authors.

<sup>2</sup> - Correction factor, K, is found by dividing the relative density of water at the test temperature by the relative density of water at 20° C.

# PARTICLE-SIZE ANALYSIS

## 1.0 Scope and Application

This method is applicable to the determination of particle-size distribution in sediment samples. Particle-size distributions are determined by a combination of sieving for particles retained on a No. 200 mesh sieve (particles with mean diameters greater than 0.074 mm or 0.0029 in) and hydrometer analysis for particles that pass through the No. 200 mesh sieve.

The method is based on a procedure in Appendix V of the U.S. Army Corps of Engineers engineering manual (1970).

## 2.0 Summary of Method

Particle-size analysis, or grain-size analysis, is a process in which a frequency distribution or a cumulative frequency distribution of discrete sized particles in a sediment sample is determined. This process is conducted by passing a known sample through a series of sieves with progressively smaller openings. The percentage of particles larger than a specific size is calculated as the weight of material retained on a sieve of that size divided by the weight of sample originally placed on the nest of sieves.

The particle-size distribution for the fraction of the original sample that passes the smallest sieve (No. 200) is determined using a hydrometer. The hydrometer method of analysis is based on Stokes' law, which relates the terminal velocity of a sphere falling freely through a fluid to the diameter. The relation is expressed according to the equation:

$$v = \frac{(\gamma_s - \gamma_f) \times D^2 \times g}{18 \eta}$$

where:

$v$  = terminal velocity of sphere, cm/sec

$\gamma_s$  = density of particle, g/cm<sup>3</sup>

$\gamma_f$  = density of fluid, g/cm<sup>3</sup>

$D$  = diameter of sphere, cm

$g$  = gravitational acceleration, cm/sec<sup>2</sup>

$\eta$  = viscosity of fluid, g/(sec × cm)

It is assumed that Stokes' law can be applied to a mass of dispersed sediment particles of various shapes and sizes. The hydrometer is used to determine the percentage of dispersed sediment particles remaining in suspension at a given time. The maximum grain size equivalent to a spherical particle is computed for each hydrometer reading using Stokes' law.

### 3.0 Interferences

Potential errors associated with the sieve analyses include the following:

1. aggregations of particles not thoroughly broken. If the material contains plastic fines, the sample should be slaked before sieving.
2. overloading sieves. This is the most common and most serious error associated with the sieve analysis and will tend to indicate that a material is coarser than it actually is. Large samples may have to be sieved in several portions and the portions retained on each sieve recombined afterwards for weighing.
3. sieves shaken for too short a period or with inadequate horizontal or jarring motions. The sieves must be shaken so that each particle is exposed to the sieve openings with various orientations and has every opportunity to fall through.
4. broken or deformed sieve screens. Sieves must be frequently inspected to ensure they contain no openings larger than the specified size for the sieve. Rips and tears commonly occur on the finer screen meshes particularly around the edge where the screen is welded to the brass frame.
5. loss of material when removing sediment from each sieve.

Potential errors associated with the hydrometer analyses include the following:

1. sediment oven-dried before test. With the exception of inorganic sediments of low dry strength, oven-drying may cause permanent changes in the particle sizes.
2. unsatisfactory type or quantity of dispersing agent. Whenever new or unusual sediments are tested, trials may be necessary to determine the type and quantity of chemical which gives the most effective dispersion and deflocculation.
3. incomplete dispersion of sediment into suspension.

4. insufficient shaking or agitating of suspension in cylinder at start of test.
5. too much sediment in suspension. The results of the hydrometer analysis will be affected in the size of the sample exceeds the approximately 150 g.
6. disturbance of suspension while inserting or removing hydrometer. Such disturbance is most likely to result when the hydrometer is withdrawn too rapidly after a reading.
7. stem of hydrometer not clean. Dirt or grease on the stem may prevent full development of the meniscus.
8. nonsymmetrical heating or cooling of suspension.
9. excessive variation in temperature of suspension during test.

Potential errors associated with the overall analyses include the following:

1. insufficient washing of material over the No. 200 sieve. The dispersing agent should be added to the water in which the sample is soaked and the sediment-water mixture should be frequently manipulated to aid the separation of particles. Coarser particles may be removed from the mixture and washed free of fines by hand to reduce the quantity of material to be washed on the sieve. While the additional water used for washing should be held to a minimum, enough must be added to insure adequate removal of the fines.
2. loss of suspension material passing the No. 200 sieve.

## 4.0 Apparatus and Materials

### 4.1 Apparatus Specific to Sieve Analyses

1. A series of U.S. standard sieves with openings ranging from 76 mm to 0.074 mm (No. 200), including a cover plate and bottom pan. Sieves with an 20 cm (8 in) diameter are generally sufficient for all particle-size analyses. The following sieves are generally used for the determination of particle-size distribution:

<u>Sieve Mesh</u>	<u>Opening Size</u> (-----mm-----)	<u>Opening Size</u> (-----in-----)
-	76	3
-	6.35	0.75
4	4.76	0.187
10	2.00	0.0787
35	0.50	0.0197
200	0.074	0.0029

Sieve sizes were selected according to the standard particle-size limits following the ASTM classification scheme (ASTM, 1985). Sieves should conform to ASTM Designation: E11, Standard Specifications for Sieves for Testing. Additional sieves may be used for testing a given sample depending upon the intended use of the particle-size distribution curve.

2. Sieve shaker, 1.25 cm vertical and lateral movement, and 500 oscillations per minute, or equivalent. Unit must accommodate a nest of sieves.
3. Paintbrush, 2.54 cm (1 in), or soft wire brush, for cleaning sieves. Brush hairs should be softer than the screen material.

#### 4.2 Apparatus Specific to Hydrometer Analyses.

1. Standard hydrometer, ASTM no. 152H or equivalent, calibrated at 20° C (68° F), graduated in grams per liter with a range of 0 to 50, respectively. The accuracy of the hydrometer should be  $\pm 1$  unit.
2. Electric stirrer. A mechanically operated stirring device (milk shake mixer) in which a suitably mounted electric motor turns a vertical shaft at a speed of not less than 10,000 rpm without load. The shaft shall be equipped with a replaceable stirring paddle of metal, plastic, or hard rubber. An acceptable stirrer is available from Soil Test, Inc., Evanston, IL, or other sources<sup>1</sup>.
3. Metal dispersion cup with internal baffles.
4. Sedimentation cylinders with a 1 L mark at  $36 \pm 2$  cm from the bottom of the inside.

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<sup>1</sup>Trade names are used solely for the purpose of providing specific information. Mention of trade names or commercial products does not constitute endorsement of recommendation for use.

5. Centigrade thermometer, range 0 to 50° C, accurate to  $\pm 0.5^\circ$  C.
6. Timing device, a watch or clock with a second hand.
7. Constant temperature bath, optional if room temperature is controlled. Either the room or bath should be controlled to  $\pm 1^\circ$  C.

#### 4.3 Apparatus for Overall Particle-Size Analyses.

1. Analytical balance, capable of weighing to 0.001 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Drying oven.
4. Thermometer, 0 to 200° C range, graduated to 1° C.
5. 600 mL glass beakers.

#### 5.0 Reagents

1. ASTM Type I water (ASTM, 1984).
2. Dispersing Agent.

Suspensions of fine grain particles will tend to flocculate (i.e., to adhere with sufficient force that they settle together as a particle of apparently larger size). Consequently, a dispersing agent is added to the sediment suspensions to prevent flocculation of the individual particles during the hydrometer analysis. The following dispersing agents, listed in approximate order of effectiveness, have been found to be satisfactory for this purpose:

- a. Sodium tripolyphosphate, 0.4 N. Dissolve 29 g solids in 1 L water.
- b. Sodium polyphosphate, 0.4 N. Dissolve 36 g solids in 1 L water.
- c. Sodium tetraphosphate, 0.4 N. Dissolve 31 g solids in 1 L water.
- d. Sodium hexametaphosphate (sodium metaphosphate), 0.4 N. Place 41 g of sodium hexametaphosphate and 2.1 g of  $\text{NaCO}_3$  in a 1 L container with approximately 900 mL water. Dilute the solution to 1 L with Type I water.

**NOTE:** Sodium hexametaphosphate is the most commonly used dispersant.

**NOTE:** Phosphate solutions are somewhat unstable and therefore should not be stored for extended periods of time. A fresh solution should be prepared at least once a month.

**NOTE:** The chemical product Calgon, available in retail outlets, should not be used as a dispersing agent as it no longer contains sodium hexametaphosphate. Also, sodium silicate should not be used as a dispersing agent since it gives unsatisfactory dispersion while at the same time permitting flocculation to a point where it is not apparent to visual examination.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Samples should be stored at 4° C between sample collection and analysis. It is recommended that particle-size samples not be frozen or oven-dried prior to analysis. Freezing-thawing cycles or sample drying may cause an irreversible change in the particle-size distribution in the sample.

All sample containers must be prewashed with detergents. If samples are to be analyzed for other parameters, acids and Type II water washings may also be required. Either glass or plastic containers can be used for the storage of samples to be analyzed for particle-size distribution.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^{\circ}$  C.

The oven should be monitored to ensure that temperature fluctuation does not exceed  $\pm 2^{\circ}$  C.

## 7.1 Hydrometer Calibration

The hydrometer must be calibrated<sup>2</sup> to establish the relationship between the true depth and the hydrometer reading using the following procedure:

1. Determine the volume of the hydrometer bulb,  $V_R$ . This may be determined in either of two ways:
  - a. Measure the volume of water displaced. Fill a 1000 mL graduated cylinder with water to approximately 700 mL. The water should be at a temperature of about 20° C. Observe and record the reading of the water level. Insert the hydrometer and again observe and record the reading. The difference in these two readings equals the volume of the bulb plus the part of the stem that is submerged. The error due to inclusion of this latter quantity is so small that it may be neglected for practical purposes.
  - b. By determining the volume from the weight of the hydrometer. Weigh the hydrometer to 0.01 g on the laboratory balance. Since the specific gravity of a hydrometer is about unity, the weight in grams may be recorded as the volume in mL. This volume includes the volume of the bulb plus the volume of the stem. The error due to inclusion of the stem volume is negligible.
2. Determine the area, in  $\text{cm}^2$ , of the graduated cylinder in which the hydrometer is to be used by measuring the distance between two graduations (measured distance should be between approximately 0.32 and 0.38 cm). The area,  $A$ , is equal to the volume included between the graduations divided by the measured distance.
3. Measure and record the distances from the lowest calibration mark on the stem of the hydrometer to each of the other major calibration marks,  $R$ , in cm.

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<sup>2</sup>ASTM hydrometers 151 H or 152 H (ASTM Designation: E 100) have a uniform size; therefore, only a single calibration is required, which can be applied to all ASTM hydrometers of this type.

4. Measure and record the distance from the neck of the bulb to the lowest calibration mark in cm. The distance,  $H_1$ , corresponding to a reading,  $R$ , equals the sum of the two distances measured in steps (3) and (4).
5. Measure the distance from the neck to the tip of the bulb. Record this as  $h$ , the height of the bulb in cm. The distance,  $h/2$ , locates the center of volume of a symmetrical bulb. If a nonsymmetrical bulb is used, the center of volume can be determined with sufficient accuracy by projecting the shape of the bulb on a sheet of paper and locating the center of gravity of this projected area.
6. Compute the true distances,  $H_R$ , corresponding to each of the major calibration marks,  $R$ , from the formula:

$$H_R = H_1 + 0.5 [h - (V_R/A)]$$

where:

$H_R$  = true distance of suspension above center of hydrometer bulb, cm

$H_1$  = distance between reading mark on hydrometer and neck of the hydrometer bulb (equals the sum of the distances measured in steps 3 and 4 above)

$h$  = distance between tip and neck of hydrometer bulb, cm

$V_R$  = volume of hydrometer,  $\text{cm}^3$  (mL)

$A$  = inside area of graduated cylinder,  $\text{cm}^2$

7. Plot the calibration curve expressing the relation between  $H_R$  and  $R$  (the hydrometer reading), with  $H_R$  on the y-axis of the graph. The relation is essentially a straight line for hydrometers having a streamlined shape.

Once calibrated, the hydrometer can generally be considered to be calibrated for the its life time of use. If the hydrometer readings in the blank start to vary by more than 2 g/L (one line of the hydrometer neck markings) and the variance can not be explained by temperature differences or differences in the composition of the dispersing agent, then a recalibration or disposal (if a crack in the glass is noticed) of the hydrometer is necessary.

## 7.2 Meniscus Correction

As part of the calibration process, a meniscus correction must be determined for each hydrometer. This is necessary because hydrometers are calibrated for the surface of the liquid but sediment suspensions must be read at the upper rim of the meniscus rather than at the surface. The meniscus correction,  $C_m$ , which is a constant for a given hydrometer, is determined by:

1. immersing the hydrometer in water.
2. observing the height to which the meniscus rises on the stem above the water surface.

For most hydrometers, it will be found that  $C_m$  is equal to approximately 0.5. This value can be assumed for routine testing.

## 8.0 Procedure

1. Transfer 50 g of the homogenized, field-moist sediment sample into a 600 mL beaker. If the sample is dominated by particle sizes finer than the No. 4 sieve, a 50 g sample is generally sufficient for these analyses. If the sample is dominated by sands, a sample size of 75 to 100 g may be needed to obtain reproducible results for the fine fraction.

However, the size of the sample to be used will depend on the maximum particle size in the sample and the requirement that the sample be representative of the material to be tested. The sample should be limited in weight so that no sieve in the series will be overloaded. Overloading of a sieve should be avoided because it can result in incomplete separation of the sample particles and subsequent errors in the particle size distribution of the sample. Maximum sieve loads on 20 cm (8 in) sieves are presented in Table 1.

The following tabulation will be used as a guide in obtaining a minimum-weight sample:

<u>Maximum Particle Size</u>	<u>Minimum Weight of Sample, g</u>
3 in.	64,000 g
2 in.	19,000 g
1.5 in.	8,000 g
1 in.	2,400 g
0.75 in.	1,000 g
0.5 in.	300 g
0.375 in.	150 g
0.187 (No. 4)	50 g

Additionally, the size of the beaker may need to be increased as the weight of the sample increases due to the presence of larger particle sizes.

**NOTE:** Highly organic sediments require special treatment and it may be necessary to oxidize the organic matter in order to perform a hydrometer analysis on these sediments. Oxidation is accomplished by mixing the sample with a solution of 30 percent hydrogen peroxide until effervescence is no longer observed. H<sub>2</sub>O<sub>2</sub> should be added in increments of 5 mL. When frothing has ceased, heat to 90° C to remove excess peroxide and water (do not take sample to dryness). If only small amounts of organic matter are present, treatment with hydrogen peroxide may be omitted.

2. Add 100 mL<sup>3</sup> of the dispersing agent and approximately 250 mL of water to the sediment. Stir and allow to stand overnight.

**NOTE:** If the sample contains more than about 10%, by weight, of sizes larger than the No. 4 sieve and more than 150 g of sample is required to obtain a representative sample (i.e., maximum particle size is greater than 0.375 in.), it is generally advisable to separate the material (after dispersing the sample - step 2) on the No. 4 sieve,

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<sup>3</sup>The original method by the U.S. Army Corps of Engineers (USACE, 1970) indicates that the addition of 15 mL of dispersing agent should be adequate for most instances. Upon addition of the dispersing agent, the suspension must be observed for reflocculation of the sample (after 2 to 3 hours). If flocculation is observed, then additional 15 mL increments must be added. To eliminate the additional time required to determine if the suspension is adequately dispersed, Gee and Bauder (1986) use a one time addition of 100 mL of dispersing agent. It is for the sake of saving time and effort that dispersion following the method of Gee and Bauder will be used here.

retaining both fractions, and recombine for the sieve analysis starting in step 13. Continue with step 3 after sieving.

3. Transfer the treated sediment to the metal dispersing cup, washing any residue from the beaker with water. Add water, if necessary, until the water surface is 5 to 7.6 cm (2 to 3 inches) below the top of the cup.
4. Mechanically mix for 5 min on electric stirrer at 10,000 rpm. Additional time may be required for highly plastic sediments (an additional 5 min is recommended for these sediments).

**NOTE:** If more than 10% of the sample is expected to be retained on the No. 4 sieve and is expected to contain less than 50 g of fines, it is generally advisable to separate the sample on a No. 4 sieve, retaining both fractions for the sieve and hydrometer analysis. To perform this separation, place the No. 4 sieve in a large funnel over the sedimentation cylinder. Quantitatively transfer the suspension from the dispersing cup to the sedimentation cylinder. Gently wash the portion of the sample retained on the No. 4 sieve using a wash bottle or gentle stream of water. Bring the suspension volume in the cylinder to approximately 800 mL. Remove the funnel and sieve. Add water until the volume of the suspension equals 1000 mL. Save the fraction retained on the No. 4 sieve and recombine with the sample in step 13. Proceed to step 6 after the suspension has had sufficient time to thermally equilibrate to the temperature expected to prevail during the test.

5. Quantitatively transfer the suspension into a 1000-mL sedimentation cylinder and add water until the volume of the suspension equals 1000 mL. The suspension should be brought to the temperature expected to prevail during the test.
6. One minute before starting the test, take the sedimentation cylinder in one hand and using a suitable rubber stopper, shake the suspension vigorously for a few seconds in order to transfer the sediment on the bottom of the cylinder into a uniform suspension. Continue the agitation for the remainder of the minute by turning the cylinder upside down and back. It may be necessary to loosen the sediment at the bottom of the cylinder by means of a glass rod before shaking to assist in the resuspension of the settled sediments.

Alternatively, the suspension may be agitated by means of a hand agitator/plunger for one minute prior to testing. A uniform distribution of the sediment particles in the suspension is accomplished by moving the hand agitator up and down through the suspension for one minute. This process also prevents the accumulation of sediment on the base and sides of the sedimentation cylinder.

**NOTE:** Add a drop of amyl alcohol if the surface of the suspension is covered with foam (Gee and Bauder, 1986).

7. Slowly immerse the hydrometer in the suspension 20 to 25 sec before each reading.

**NOTE:** Care should be taken when inserting and removing the hydrometer to prevent disturbance of the suspension.

8. Observe and record the hydrometer readings after 1 and 2 min have elapsed from the time the mixing (either by cylinder inversion or plunging) has been completed. After the 2 min reading, carefully remove the hydrometer from the suspension and place it in a graduated cylinder of clean water). (If a hydrometer is left in a sediment suspension for any length of time, material will settle on or adhere to the hydrometer bulb and this will cause a significant error in the reading).

**NOTE:** Make all hydrometer readings at the top of the meniscus.

9. At the end of 2 min and after each subsequent hydrometer reading, place a thermometer in the suspension and record the temperature. The temperature should be recorded to  $\pm 0.5^{\circ}$  C. Temperature changes of the sediment suspension during the test will affect the test results. Variations in temperature should be minimized by keeping the suspension away from heat sources such as radiators, sunlight, or open windows. A constant-temperature bath or constant temperature room provide convenient means for controlling temperature variation effects. Temperatures should be controlled within  $\pm 1^{\circ}$  C.

10. Insert the hydrometer in the suspension and record readings after elapsed times of 4, 15, 30, 60, 120<sup>4</sup>, 240, and 1440 min, removing the hydrometer from the suspension after each reading and placing it in a graduated cylinder of clean water.
11. Quantitatively transfer the sediment and suspension from the 1000 mL sedimentation cylinder to a 200-mesh (0.074 mm) sieve using a wash bottle or gentle stream of water.
12. Gently wash the sands and other coarser particles until all the fines have passed through the 200-mesh sieve.

**NOTE:** The disposal of the fine fraction should be performed according to State regulations.

13. Transfer the sample to a tared beaker.
14. Oven-dry the sample at 103 to 105° C, allow to cool, and weigh. If the sample weighs less than 500 g, weigh it to the nearest 0.1 g. If the sample weighs over 500 g, weigh to the nearest 1 g. Record the dry weight of the sample.
15. Arrange the nest of sieves according to size with decreasing opening diameters from top to bottom. Attach the bottom pan to the bottom of the smallest sieve opening diameter used.
16. Place the sample on the top sieve of the nest and put the cover plate over the top sieve.
17. Place the nest of sieves in the shaking machine and shake for 10 min, or until additional shaking does not produce appreciable changes in the amounts of material on each sieve.

If a shaking machine is not available, the nest of sieves may be shaken by hand. In the hand operation, shake the nest of sieves with a lateral and vertical motion, accompanied by jarring, to keep the material moving continuously over the surfaces of the sieves. Jarring is accomplished by occasionally dropping the nest lightly on several thicknesses of magazines/papers. The nest should not be broken to rearrange particles or to manipulate them through a sieve by hand. Hand-shaking should be continued for at least 15 min.

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<sup>4</sup>A final reading after 120 min is sufficient for most soils when hydrometer analysis is used for classification purposes. Additional readings at 240 and 1440 min may be made to further separate the fines into individual silt and clay fractions.

18. Remove the nest of sieves from the mechanical shaker, if used. Beginning with the top sieve, transfer the contents of the sieve to a piece of heavy paper approximately 30 cm<sup>2</sup> (1 ft<sup>2</sup>). Carefully invert the sieve on the paper and gently brush the bottom of the sieve to remove all the sample.
19. Transfer the sample from the paper to the balance and weigh in accordance with requirements in step 14. Record the weight of material retained on each sieve to the nearest 0.001 g.

**NOTE:** Care should be exercised that no loss of material occurs during the transfer.

20. Repeat steps 18 and 19 for each sieve.

## 9.0 Quality Control

### 9.1 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 10 percent or less.

**NOTE:** Precision for the coarser fractions naturally tends to be more variable than for the finer fractions due to fewer particles accounting for the weight of these fractions. Therefore, precision for the largest particle sizes may not meet the acceptance criterion. However, the whole analysis (i.e., all fractions) should be examined to determine if acceptable precision has been obtained with a majority of the fractions should meet the acceptance criterion.

### 9.2 Blanks

The addition of a dispersing agent to the sediment suspension results in an increase in density of the liquid and necessitates a correction to the observed hydrometer reading. The correction factor,  $C_d$ , is determined by adding to a 1000 mL sedimentation cylinder partially filled with water, 100 mL of dispersing agent, filling the cylinder to the 1000 mL mark with water, inserting the hydrometer, and observing the reading. The correction factor,  $C_d$ , is equal to the difference between this reading and the hydrometer reading in pure water (i.e., no dispersing agent added).

One blank should be prepared and analyzed for each batch of dispersing agent to account for the slight differences in dispersing agent concentrations and resultant density changes.

### 9.3 Internal Consistency Checks

The sum of the weights retained on each sieve should equal the weight of the coarse fraction obtained in steps 13 and 14 within  $\pm 1\%$ . If the difference is greater than 1 percent, sample processing should be discontinued until the source of the error is identified and a decision made to repeat the analyses.

## 10.0 Method Performance

None identified.

## 11.0 Calculations

### 11.1 Percent Retained on No. 200 Sieve

Compute the percentage retained on the No. 200 sieve for the total sample used in the sieve and hydrometer combined analysis as follows:

$$\text{Percent retained on No. 200 sieve, \%} = \frac{W_d \times 100}{B \times [(1-C)/(100+C)]}$$

where:

$W_d$  = dry weight of sample retained on No. 200 sieve from steps 13 and 14, g

$B$  = weight of field-moist sample, g

$C$  = moisture content as determined by previous method, %

### 11.2 Sieve Analysis Calculations

The percentage of material by weight retained on the various sieves is computed as follows:

$$\text{Percent retained, \%} = \frac{A \times 100}{B \times [(1-C)/(100+C)]}$$

where:

A = weight of fraction retained on the sieve, g

B = weight of field-moist sample, g

C = moisture content as determined by previous method, %

### 11.3 Hydrometer Analysis Calculations

Compute the corrected hydrometer readings, R, for use in computing particle diameter by adding the meniscus correction,  $C_m$ , to the actual hydrometer readings,  $R'$ . Record the corrected reading, R.

Calculate the particle diameter corresponding to a given hydrometer reading on the basis of Stokes' equation, using the nomograph shown in Fig. 1 (nomograph). The R-scale corresponding to the distances  $H_R$  is prepared using the hydrometer calibration curves as determined in section 7.0 - step 6. The R-scale should be designed for the particular hydrometer used in the test. A key showing the steps to follow in computing D for various values of R is shown on the chart. Record the particle diameters, D, for each time interval of sampling.

To calculate the percent finer by weight, use the following formula:

$$\text{Percent finer by weight} = \frac{(R - C_d + m) \times 100}{B \times [(1-C)/(100+C)]}$$

where:

R = corrected hydrometer reading from the hydrometer calibration chart

$C_d$  = dispersing agent correction factor from section 9.2

m = temperature correction factor from Table 2.

B = weight of field-moist sample, g

C = moisture content as determined by previous method, %

**NOTE:** Calculations for routine work can be greatly facilitated by using charts, tables, and other simplifying aids based on a given oven-dry weight of the sample and average specific gravity values for the major sediment types.

The results of the particle-size analysis, in terms of particle diameter and total percent finer by weight, are generally presented either in the form of particle-size distribution curves on a semi-logarithmic chart or as tables. The particle-size distribution curves obtained from the sieve and hydrometer analyses are joined by constructing a smooth curve between all points.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

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Plumb, R.H., Jr. 1981. Procedure for Handling and Chemical Analysis of Sediment and Water Samples. Technical Report EPA/CE-81-1. U.S. Army Engineering Waterways Experiment Station, Vicksburg, MS.

U.S. Army Corps of Engineers. 1970. Grain-Size Analysis. *In* Engineering Manual, Laboratory Soils Testing. EM 1110-2-1906. Compiled by Headquarters, Department of the Army, Office of the Chief Engineer. Updated by Change 1, May 1, 1980 and Change 2, August 29, 1986.

Table 1. Maximum Sieve Loads on 20 cm Sieves (after Plumb, 1981).

<u>Sieve Mesh</u>	<u>Opening Size</u> (-----mm-----)	<u>Maximum Load</u> (-----g-----)
-	76	N/A <sup>a</sup>
-	6.35	200
4	4.76	175.
10	2.00	110.
35	0.50	60
200	0.074	25

a - N/A = not applicable due to large individual particle size.

Table 2. Temperature Correction Factor, m, for Use in Computing Percent Finer.

<u>Degrees</u> <u>(C)</u>	<u>Degrees</u> <u>(F)</u>	<u>Correction</u>	<u>Degrees</u> <u>(C)</u>	<u>Degrees</u> <u>(F)</u>	<u>Correction</u>
14.0	57.2	-0.9	24.5	76.1	+0.9
14.5	58.1	-0.8	25.0	77.0	+1.0
15.0	59.0	-0.8	25.5	77.9	+1.1
15.5	59.9	-0.7	26.0	78.8	+1.3
16.0	60.8	-0.6	26.5	79.7	+1.4
16.5	61.7	-0.6	27.0	80.6	+1.5
17.0	62.6	-0.5	27.5	81.5	+1.6
17.5	63.5	-0.4	28.0	82.4	+1.8
18.0	64.4	-0.4	28.5	83.3	+1.9
18.5	65.3	-0.3	29.0	84.2	+2.1
19.0	66.2	-0.2	29.5	85.1	+2.2
19.5	67.1	-0.1	30.0	86.0	+2.3
20.0	68.0	0.0	30.5	86.9	+2.5
20.5	68.9	+0.1	31.0	87.8	+2.6
21.0	69.8	+0.2	31.5	88.7	+2.8
21.5	70.7	+0.3	32.0	89.6	+2.9
22.0	71.6	+0.4	32.5	90.5	+3.0
22.5	72.5	+0.5	33.0	91.4	+3.2
23.0	73.4	+0.6	33.5	92.3	+3.3
23.5	74.3	+0.7	34.0	93.2	+3.5
24.0	75.2	+0.8			

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# AMMONIA NITROGEN IN SEDIMENTS (COLORIMETRIC, AUTOMATED)

## 1.0 Scope and Application

This method covers the determination of ammonia in sediments. Ammonia is distilled from a sediment slurry and determined with an automated colorimetric method. This range is for photometric measurements made at 630-660 nm in a 15 mm or 50 mm tubular flow cell. Higher concentrations can be determined by sample dilution. Approximately 20 to 60 samples per hour can be analyzed.

This procedure is based on Method 350.1 (APHA, 1989).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

Ammonia is distilled from a sediment-distilled water slurry and trapped in a boric acid solution. The distillate is analyzed with an automated method in which alkaline phenol and hypochlorite are reacted with ammonia to form indophenol blue. The blue color formed is intensified with sodium nitroprusside and is proportional to the ammonia concentration. The intensity of the color is automatically determined by measuring sample absorbance at 630 nm.

## 3.0 Interferences

Sulfide that may be present in sediments can interfere with ammonia analysis. This interference can be reduced or eliminated by boiling the acidified sediment slurry prior to distilling off the ammonia under neutral conditions (Section 8.5). The sulfide interference can also be removed by precipitation with lead carbonate.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.

2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Technicon AutoAnalyzer Unit (AAI or AAI) consisting of:
  - a. sampler,
  - b. manifold (AAI) or analytical cartridge (AAI),
  - c. proportioning pump,
  - d. heating bath with double delay coil (AAI),
  - e. colorimeter equipped with 15 mm tubular flow cell and 630-660 nm filters,
  - f. recorder, and
  - g. digital printer for AAI (optional).
4. Kjeldahl digestion apparatus.

## 4.2 Materials

1. Boiling chips
2. Erlenmeyer flask, 1 L.
3. Erlenmeyer flask, 100 mL.
4. Kjeldahl flask, 800 mL.
5. Volumetric flask, class A, 100 mL.
6. Volumetric flask, class A, 1 L.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.

**NOTE:** Type II water: Special precaution must be taken to insure that this Type II water is free of ammonia. Such water is prepared by passage of Type II water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. The regeneration of the ion exchange column should be carried out according to the instruction of the manufacturer. All solutions must be made using ammonia-free Type II water.

2. Boric acid solution. Dissolve 20 g anhydrous boric acid ( $H_3BO_3$ ) in ammonia-free Type II water. Dilute to 1 liter with Type II water.

3. Disodium ethylenediamine-tetraacetate (EDTA), 5%. Dissolve 50 g of EDTA (disodium salt) and approximately six pellets of NaOH in 1 liter of Type II water.
4. Phosphate buffer solution, pH 7.4. Dissolve 14.3 g anhydrous potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ), and 68.8 g anhydrous dipotassium hydrogen phosphate ( $\text{K}_2\text{HPO}_4$ ). Dilute to 1 liter with ammonia-free Type II water.
5. Sodium hypochlorite ( $\text{NaOCl}$ ) solution. Dilute 250 mL of a bleach solution containing 5.25% NaOCl (such as "Clorox") to 500 mL with Type II water. Available chlorine level should approximately 2 to 3%.

**NOTE:** Since "Clorox" is a proprietary product, its formulation is subject to change. The analyst must remain alert to detecting any variation in this product significant to its use in this procedure. Due to the instability of this product, storage over an extended period should be avoided.

6. Sodium hydroxide ( $\text{NaOH}$ ), 1 N: Dissolve 40 g NaOH in ammonia-free Type II water. Dilute to 1 liter with Type II water.
7. Sodium nitroprusside ( $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot\text{H}_2\text{O}$ ), 0.05%. Dissolve 0.5 g of sodium nitroprusside in 1 liter of Type II water.
8. Sodium phenolate. Using a 1 liter Erlenmeyer flask, dissolve 83 g phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) in 500 mL of Type II water. In small increments, cautiously add with agitation, 32 g of NaOH. Periodically cool flask under water faucet. When cool, dilute to 1 liter with Type II water.
9. Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ), reagent grade. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
10. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), 5 N, for use as the air scrubber solution. Carefully add 139 mL of concentrated sulfuric acid to approximately 500 mL of ammonia-free Type II water. Cool to room temperature and dilute to 1 liter with ammonia-free Type II water.
11. Ammonia stock solution. Dissolve 3.819 g of anhydrous ammonium chloride ( $\text{NH}_4\text{Cl}$ ), dried at  $105^\circ\text{C}$ , in Type II water. Dilute to 1 liter with Type II water. (1.0 mg/mL  $\text{NH}_3\text{-N}$ ).
12. Standard solution A. Dilute 10.0 mL of ammonia stock solution to 1 liter with Type II water. (0.01 mg/mL  $\text{NH}_3\text{-N}$ ).
13. Standard solution B. Dilute 10.0 mL of standard solution A to 1 liter with Type II water. (0.001 mg/mL  $\text{NH}_3\text{-N}$ ).

## 6.0 Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Samples should be stored in a field moist condition which should help minimize the possible loss of ammonia by volatilization. In addition, samples should be processed within a week to minimize possible losses of ammonia due to volatilization or transformation.

A holding time of 28 days after sample collection is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of sediment samples to be analyzed for ammonia.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Using standard solutions A and B, prepare the following standards in 100 mL volumetric flasks (prepare fresh daily):

NH<sub>3</sub>-N, mg/L                      mL Standard Solution/100 mL

Solution B

0.01	1.0
0.02	2.0
0.05	5.0
0.10	10.0

Solution A

0.20	2.0
0.50	5.0
0.80	8.0
1.00	10.0
1.50	15.0
2.00	20.0

## 8.0 Procedure

### 8.1 Preparation of Equipment

1. Add 500 mL of Type II water to an 800 mL Kjeldahl flask.

**NOTE:** The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping.

2. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.

### 8.2 Sample Distillation

1. Weigh a 0.5 to 1.0 g sample of homogenized, field-moist sediment and quantitatively transfer the sample to a 100 mL Erlenmeyer flask
2. Add approximately 50 ml ammonia-free Type II water and 3 to 4 drops concentrated sulfuric acid.

**NOTE:** Addition of a few drops of concentrated sulfuric acid will stabilize the ammonia. The procedure can be interrupted at this point, if necessary.

3. Transfer the acidified sediment slurry to a 800 mL Kjeldahl flask.
4. Add 500 mL ammonia-free Type II water and a few boiling stones to an 800 mL Kjeldahl flask.
5. Boil the sample for a few minutes to remove any sulfides that may be present.

**NOTE:** This step will also remove any volatile organics such as formaldehyde that may interfere with the Nesslerization determination of ammonia.

**NOTE:** Sulfide interferences may also be removed by precipitating the sulfide with lead carbonate.

6. Neutralize the pH of the sediment slurry with 1 N NaOH to a pH of about 6.6.
7. Add 10 mL phosphate buffer.
8. Distill over 300 mL of sample, at a rate of 6 to 10 mL/minute, and collect in 50 mL boric acid solution.
9. Dilute the final distillate to 500 mL with ammonia free water. The samples are now ready for analysis.

### 8.3 Automated Colorimetric Analysis

**NOTE:** The intensity of the color developed between ammonia and the colorimetric reagents is pH dependent. In order to compensate for this effect, the pH of the samples, the standard ammonia solutions, and the wash water should be similar. This can be accomplished by either (1) adding 2 mL concentrated  $H_2SO_4$  per liter to the standards and wash water or (2) neutralizing the pH of the samples with NaOH or KOH.

1. Select the appropriate manifold for the automated analyses to be run. For a working range of 0.01 to 2.00 mg  $NH_3$ -N/L use the AAI set up. For a working range of 0.01 to 1.0 mg  $NH_3$ -N/L, use the AAll set up. Higher concentrations may be accommodated by sample dilution.

**NOTE:** Manifold flow rates for the AAI set up are as follows:

Wash Water	2.0 mL/min.
Sample	0.42 mL/min.
EDTA	0.8 mL/min.
Air*	0.23 mL/min.
Na-phenolate	0.42 mL/min.
Na-hypochlorite	0.32 mL/min.
Na-nitroprusside	0.42 mL/min.

**NOTE:** Manifold flow rates for the AAll set up are as follows:

Wash Water	2.9 mL/min.
Sample	2.0 mL/min.
EDTA	0.8 mL/min.
Air*	2.0 mL/min.
Na-phenolate	0.6 mL/min.
Na-hypochlorite	0.6 mL/min.
Na-nitroprusside	0.6 mL/min.

\* = air should be scrubbed through 5 N H<sub>2</sub>SO<sub>4</sub>

2. Allow both colorimeter and recorder to warm up for 30 minutes.
3. Obtain a stable baseline with all reagents, feeding Type II water through sample line.
4. For the AAI system, sample at a rate of 20/hr. 1:1. For the AAll, use a 60/hr 6:1 cam with a common wash.
5. Arrange ammonia standards in the sampler in order of decreasing ammonia concentration.
6. Complete loading of the sampler tray with routine and quality assurance/quality control samples.
7. Switch sample line from distilled water to sampler and begin analysis.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for ammonia in sediments is 100 µg/kg.

## 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured ammonia concentrations.

## 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

## 9.4 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 10.0 Method Performance

In a single laboratory (EMSL-CIN), using surface water samples at concentrations of 1.41, 0.77, 0.59 and 0.43 mg NH<sub>3</sub>-N/L, the standard deviation was  $\pm 0.005$ . In a second single laboratory study (Alberta Pollution Control Laboratory), the calculated coefficient of variation for surface water samples with ammonia concentrations of 0.029, 0.060, and 0.093 mg/L NH<sub>3</sub>-N were 4.7, 2.0, and 1.1%, respectively.

In a single laboratory (EMSL-CIN), using surface water samples at concentrations of 0.16 and 1.44 mg NH<sub>3</sub>-N/L, recoveries were 107 and 99%, respectively. In a second single laboratory study (Alberta Pollution Control Laboratory), using surface water samples with NH<sub>3</sub>-N concentrations of 0.008, 0.015, and 0.039 mg/L, the recoveries were 104, 97, and 105%, respectively.

## 11.0 Calculations and Reporting

The resultant ammonia concentrations can be obtained by comparison of distillate peak heights to the standard curve of peak heights of the standards plotted against their corresponding known concentration values. The ammonia concentration of the original field moist sample is then calculated as:

$$\text{Ammonia nitrogen, mg/kg (wet weight)} = \frac{X \times Y \times 1000}{g}$$

where:

X = ammonia concentration in distillate, mg/L

Y = final volume of sediment distillate, L

g = wet weight of sediment sample, g

## 12.0 References

Alberta Environmental Centre. 1981. Methods Manual for Chemical Analysis of Water and Wastes. Environment Canada, Vegreville, Alberta, Canada.

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# AMMONIA NITROGEN IN SEDIMENTS (COLORIMETRIC, MANUAL)

## 1.0 Scope and Application

This method covers the determination of ammonia in sediments. Ammonia is distilled from a sediment slurry and determined colorimetrically. Spectrophotometric measurements are made at a wavelength of 425 nm. The ammonia concentrations determined by this method should be  $\leq 1.0$  mg NH<sub>3</sub>-N/L. Higher concentrations can be determined by sample dilution.

This procedure is based on Method 350.2 (APHA, 1989).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

Ammonia is distilled from a sediment-distilled water slurry and trapped in a boric acid solution. The distillate is analyzed after nesslerization using a spectrophotometer. The intensity of the color is automatically determined by measuring sample absorbance at 425 nm.

## 3.0 Interferences

Sulfide that may be present in sediments can interfere with ammonia analysis. This interference can be reduced or eliminated by boiling the acidified sediment slurry for a few minutes prior to distilling off the ammonia under neutral conditions (Section 8.5). The sulfide interference can also be removed by precipitation with lead carbonate.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Kjeldahl distillation apparatus.

4. Spectrophotometer or filter photometer for use at 425 nm and providing a light path of 1 cm or more.

## 4.2 Materials

1. Boiling chips
2. Erlenmeyer flask, 100 mL.
3. Kjeldahl flask, 800 mL.
4. Nessler tubes. Matched Nessler tubes (APHA Standard) about 300 mm long, 17 mm inside diameter, and marked at 225 mm  $\pm$  1.5 mm inside measurement from bottom.
5. Volumetric flask, class A, 100 mL.
6. Volumetric flask, class A, 1 L.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.

**NOTE:** Type II water: Special precaution must be taken to insure that this Type II water is free of ammonia. Such water is prepared by passage of Type II water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. The regeneration of the ion exchange column should be carried out according to the instruction of the manufacturer. All solutions must be made using ammonia-free Type II water.

2. Boric acid solution, 2%. Dissolve 20 g anhydrous boric acid ( $H_3BO_3$ ) in ammonia-free Type II water. Dilute to 1 liter with Type II water.
3. Nessler reagent. Dissolve 100 g of mercuric iodide (HgI) and 70 g of potassium iodide (KI) in a small amount of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 mL of Type II water. Dilute to 1 liter with Type II water.

**NOTE:** If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.

**NOTE:** This reagent should give the characteristic color with ammonia within 10 minutes after addition and should not produce a precipitate with small amounts of ammonia ( $\leq 0.04$  mg/50 mL).

4. Phosphate buffer solution, pH 7.4. Dissolve 14.3 g anhydrous potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ), and 68.8 g anhydrous dipotassium hydrogen phosphate ( $\text{K}_2\text{HPO}_4$ ). Dilute to 1 liter with ammonia-free Type II water.
5. Sodium hydroxide (NaOH), 1 N: Dissolve 40 g NaOH in ammonia-free Type II water. Dilute to 1 liter with Type II water.
6. Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ), reagent grade. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration  $< \text{MDL}$ , then the acid can be used.
7. Ammonia stock solution. Dissolve 3.819 g of anhydrous ammonium chloride ( $\text{NH}_4\text{Cl}$ ), dried at  $105^\circ \text{C}$ , in Type II water. Dilute to 1 liter with Type II water. (1.0 mg/mL  $\text{NH}_3\text{-N}$ ).
8. Ammonia standard solution. Dilute 10.0 mL of ammonia stock solution to 1 liter with Type II water. (0.01 mg/mL  $\text{NH}_3\text{-N}$ ).

## 6.0 Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Samples should be stored in a field moist condition which should help minimize the possible loss of ammonia by volatilization. In addition, samples should be processed within a week to minimize possible losses of ammonia due to volatilization or transformation.

A holding time of 28 days after sample collection is generally cited for this parameter.

Samples should be stored under refrigerated conditions ( $4^\circ \text{C}$ ).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of sediment samples to be analyzed for ammonia.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Prepare a series of Nessler tube standards as follows:

<u>mL of Standard</u> <u>(0.01 mg/mL NH<sub>3</sub>-N)</u>	<u>mg NH<sub>3</sub>-N/50.0 mL</u>
0.0	0.0
0.5	0.005
1.0	0.01
2.0	0.02
3.0	0.03
4.0	0.04
5.0	0.05
8.0	0.08
10.0	0.10

Dilute each tube to 50 mL with Type II water. Add 2.0 mL of Nessler reagent. Mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained, plot absorbance vs. mg NH<sub>3</sub>-N for the standard curve.

The sulfuric acid standard solution must be standardized following one of the two following methods:

- Standardize the approximately 0.02 N acid against 0.0200 N Na<sub>2</sub>CO<sub>3</sub> solution. This sodium carbonate solution is prepared by dissolving 1.060 g anhydrous Na<sub>2</sub>CO<sub>3</sub>, oven-dried at 140° C, and diluting to 1 liter with CO<sub>2</sub>-free Type II water.
- Standardize the approximately 0.1 N H<sub>2</sub>SO<sub>4</sub> solution against a 0.100 N Na<sub>2</sub>CO<sub>3</sub> solution. By proper dilution, the 0.02 N acid can then be prepared.

The later method (b.) is preferable.

## 8.0 Procedure

### 8.1 Preparation of Equipment

1. Add 500 mL of Type II water to an 800 mL Kjeldahl flask.

**NOTE:** The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping.

2. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.

### 8.2 Sample Distillation

1. Weigh a 0.5 to 1.0 g sample of homogenized, field-moist sediment and quantitatively transfer the sample to a 100 mL Erlenmeyer flask
2. Add approximately 50 ml ammonia-free Type II water and 3 to 4 drops concentrated sulfuric acid.

**NOTE:** Addition of a few drops of concentrated sulfuric acid will stabilize the ammonia. The procedure can be interrupted at this point, if necessary.

3. Transfer the acidified sediment slurry to a 800 mL Kjeldahl flask.
4. Add 500 mL ammonia-free Type II water and a few boiling stones to an 800 mL Kjeldahl flask.
5. Boil the sample for a few minutes to remove any sulfides that may be present.

**NOTE:** This step will also remove any volatile organics such as formaldehyde that may interfere with the Nesslerization determination of ammonia.

**NOTE:** Sulfide interferences may also be removed by precipitating the sulfide with lead carbonate.

6. Neutralize the pH of the sediment slurry with 1 N NaOH to a pH of about 6.6.
7. Add 10 mL phosphate buffer.
8. Distill over 300 mL of sample, at a rate of 6 to 10 mL/minute, and collect in 50 mL boric acid solution.
9. Dilute the final distillate to 500 mL with ammonia free water. The samples are now ready for analysis.

### 8.3 Colorimetric Analysis

1. Allow the spectrophotometer to warm up for 30 minutes.
2. Add 2.0 mL of Nessler reagent to 50 mL of the distillate in a Nessler tube. Mix.
3. After 20 minutes, read the absorbance at 425 nm.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for ammonia in sediments is 100 µg/kg.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured ammonia concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be ± 15% of the known value or within the certified value provided by the supplier, whichever is larger.

## 9.4 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 10.0 Method Performance

In a single laboratory (EMSL-CIN), using surface water samples at concentrations of 1.41, 0.77, 0.59 and 0.43 mg NH<sub>3</sub>-N/L, the standard deviation was  $\pm 0.005$ . In a second single laboratory study (Alberta Pollution Control Laboratory), the calculated coefficient of variation for surface water samples with ammonia concentrations of 0.029, 0.060, and 0.093 mg/L NH<sub>3</sub>-N were 4.7, 2.0, and 1.1%, respectively.

In a single laboratory (EMSL-CIN), using surface water samples at concentrations of 0.16 and 1.44 mg NH<sub>3</sub>-N/L, recoveries were 107 and 99%, respectively. In a second single laboratory study (Alberta Pollution Control Laboratory), using surface water samples with NH<sub>3</sub>-N concentrations of 0.008, 0.015, and 0.039 mg/L, the recoveries were 104, 97, and 105%, respectively.

## 11.0 Calculations and Reporting

The resultant ammonia concentrations can be obtained by comparison of distillate peak heights to the standard curve of peak heights of the standards plotted against their corresponding known concentration values. The ammonia concentration of the original field moist sample is then calculated as:

$$\text{Ammonia nitrogen, mg/kg (wet weight)} = \frac{X \times Y \times 1000}{g}$$

where:

X = ammonia concentration in distillate, mg/L

Y = final volume of sediment distillate, L

g = wet weight of sediment sample, g

## 12.0 References

Alberta Environmental Centre. 1981. Methods Manual for Chemical Analysis of Water and Wastes. Environment Canada, Vegreville, Alberta, Canada.

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. Method 4500-NH<sub>3</sub> H. 17th Edition, APHA, New York, New York. p. 4-126.

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

# CYANIDE IN SEDIMENTS (COLORIMETRIC, AUTOMATED UV)

## 1.0 Scope and Application

This method is used to determine the concentration of inorganic cyanide in sediments. The method detects inorganic cyanides that may be present as either simple soluble salts or complex radicals.

The colorimetric method is sensitive to approximately 0.02 mg/L of cyanide and is recommended for concentrations below 1 mg/L. The range of the procedure can be adjusted by modifying the sample preparation technique or the cell path length. However, the amount of sodium hydroxide in the standards and the sample to be analyzed must be the same.

This procedure is based on SW-846 Method 9012 (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

An aliquot of the sediment sample to be analyzed is placed in 500 mL of acidified distilled water. The resulting suspension is heated to distill hydrocyanic acid (HCN) from the acidic suspension and into a sodium hydroxide trap. The cyanide concentration of the final distillate is determined with an automated UV colorimetric procedure.

Cyanide in the distillate is reacted with chloramine-T at a pH less than 8 to produce cyanogen chloride (CNCl). After this reaction is complete, the addition of pyridine-barbituric acid reagent produces a red-blue color that is proportional to the cyanide concentration. The intensity of the color is automatically determined by measuring sample absorbance at 570 nm. The concentration of NaOH must be the same in the standards, the sample distillate, and any dilutions of the original sample distillate to obtain colors of comparable intensity.

### 3.0 Interferences

Sulfides adversely affect the development of color in the analytical procedure. This interference can be reduced or eliminated by adding bismuth nitrate to the samples to precipitate the sulfide prior to distillation (Section 8.1.4). Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce sulfide during the distillation procedure should also be treated with bismuth nitrate prior to distillation.

Nitrate and/or nitrite in samples can act as a positive interference when present at concentrations above 10 mg/L and in the presence of certain organic compounds. These nitrogen compounds can form nitrous acid during the distillation process which will react with some organic compounds to form oxides. These oxides will decompose under conditions developed in the colorimetric procedure to generate HCN. This interference is eliminated by treating the samples with sulfamic acid prior to distillation (Section 8.1.5).

### 4.0 Apparatus and Materials

#### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Reflux distillation apparatus. The boiling flask should be of 1-liter size with inlet tube and provision for condenser. The gas absorber is a Fisher-Milligan scrubber (Fisher Catalog #07-513), or equivalent.
4. Automated continuous-flow analytical instrument with:
  - a. sampler,
  - b. manifold with UV digester,
  - c. proportioning pump,
  - d. heating bath with distillation coil,
  - e. distillation head,
  - f. colorimeter equipped with a 15 mm flow cell and 570 nm filter, and
  - g. recorder.
5. Extractor. Any suitable device that sufficiently agitates a sealed container with a capacity of one liter or more. For the purpose of this procedure, agitation must be sufficient to: (1) maintain

continuous contact between all sample particles and the extraction fluid, and (2) prevent stratification of the sample and the extraction fluid.

6. Buchner funnel, 500 mL capacity.
7. Vacuum filtration flask, 1 L.
8. Glass fiber filter pads.
9. Vacuum source, preferably a water driven aspirator. A valve or stopcock is needed to release the vacuum.
10. Top loading balance, capable of weighing 0.1 g.

## 4.2 Materials

1. Potassium iodide-starch test paper.
2. Volumetric flasks, class A, 250 mL.
3. Volumetric flasks, class A, 100 mL.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Ascorbic acid ( $C_6H_8O_6$ ), analytical reagent grade crystals.
3. Bismuth nitrate solution ( $Bi(NO_3)_3$ ). Dissolve 30.0 grams of  $Bi(NO_3)_3$  in 100 mL of Type II water. While stirring, add 250 mL of glacial acetic acid. Stir until dissolved. Dilute to 1 liter with Type II water.
4. Chloramine-T solution. Dissolve 1.0 g of white, water-soluble, chloramine-T in 100 mL of Type II water. Refrigerate until ready to use.
5. Concentrated acetic acid ( $C_4H_6O_3$ ), glacial, reagent grade. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
6. Concentrated sulfuric acid ( $H_2SO_4$ ), reagent grade. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
7. Sulfuric acid (1:1). Slowly add 500 mL of concentrated  $H_2SO_4$  to 500 mL of Type II water.

**CAUTION:** This is an exothermic reaction.

8. Magnesium chloride solution ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ). Dissolve 510 g of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  into a 1 liter flask. Dilute to 1 liter with Type II water.
9. Pyridine-barbituric acid reagent. Place 15 g of barbituric acid ( $\text{C}_4\text{H}_4\text{O}_3\text{N}_2$ ) in a 250 mL volumetric flask. Add just enough Type II water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine ( $\text{C}_5\text{H}_5\text{N}$ ) and mix. Add 15 mL of concentrated HCl. Allow to cool to room temperature. Dilute to 250 mL with Type II water. This reagent is stable for approximately six months, if stored in a cool, dark place.
10. Sodium dihydrogenphosphate ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ), 1 M. Dissolve 138 g of  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  in 1 liter of Type II water.
11. Sodium hydroxide solution (NaOH), 1.25 N. Dissolve 50 g of NaOH in Type II water. Dilute to 1 liter with Type II water.
12. Sodium hydroxide solution (NaOH), 1 N. Dissolve 40 g of NaOH in Type II water. Dilute to 1 liter with Type II water.
13. Sodium hydroxide dilution water and receptacle wash water (NaOH), 0.25 N. Dissolve 10.0 g NaOH in 500 mL of Type II water. Dilute to 1 liter with Type II water.
14. Sulfamic acid solution ( $\text{NH}_2\text{SO}_3\text{H}$ ). Dissolve 40 g of sulfamic acid in Type II water. Dilute to 1 liter with Type II water.
15. Cyanide stock solution. Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of Type II water. Standardize with 0.0192 N  $\text{AgNO}_3$ . Dilute to appropriate concentration of 1 mg/mL.
16. Intermediate standard cyanide solution. Dilute 100.0 mL of stock cyanide solution to 1 liter with Type II water (100  $\mu\text{g}/\text{mL}$  CN).
17. Working standard cyanide solution. Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1 liter with Type II water (10.0  $\mu\text{g}/\text{mL}$  CN). Store in a glass-stoppered bottle.

**NOTE:** All working standards should contain 2 mL of 1 N NaOH per 100 mL.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Since field-moist samples are used in the determination, preservation of the sample is not practical. Therefore, analysis should begin as soon as possible after sample collection. A holding time of 14 days is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of aqueous samples to be analyzed for cyanide.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Two methods are given for preparing a standard cyanide curve. Section 7.1 should be followed if the samples do not contain sulfide and Section 7.2 should be followed if the samples to be analyzed contain sulfide. The difference between these two methods is that all the cyanide standards must be carried through the sample distillation process when sulfide is present.

### 7.1 Standard Curve for Samples without Sulfide.

1. Prepare a series of standards by pipetting suitable volumes of the working standard cyanide solution into 250 mL volumetric flasks. To each standard add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with Type II water. Prepare as follows:

<u>mL of Working Standard Solution</u> <u>(1 mL = 10 µg CN)</u>	<u>Concentration</u> <u>(µg CN/250 mL)</u>
0.0	BLANK
1.0	10
2.0	20
5.0	50
10.0	100
15.0	150
20.0	200

It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and a low) be distilled and compared with similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within  $\pm 10\%$  of the undistilled standards, the analyst should find the cause of the apparent error before proceeding.

2. Prepare a standard curve by plotting absorbances of standards vs. cyanide concentrations.
3. To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard cyanide solution or the working standard cyanide solution to 500 mL of sample to ensure a level of 20  $\mu\text{g/L}$ . Proceed with the analysis as in Section 8.1 - Sample Distillation.

## 7.2 Standard Curve for Samples with Sulfide

1. All standards must be distilled in the same manner as the samples. A minimum of three standards shall be distilled.
2. Prepare a standard curve by plotting absorbance of standards vs. cyanide concentration.

## 8.0 Procedure

### 8.1 Sample Distillation

1. Weigh a 1 to 5 g aliquot of the homogenized field-moist sample and quantitatively transfer the sample to a 1 liter boiling flask containing 500 mL ASTM Type II water.
2. Pipet 50 mL of 1.25 N sodium hydroxide solution into the absorbing tube of the reflux distillation apparatus. Connect the boiling flask, condenser, absorber, and trap in the train.
3. Adjust the vacuum source to allow a slow stream of air to enter the boiling flask. Approximately two bubbles of air per second should enter the boiling flask.
4. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper.

**NOTE:** If test is positive, treat the sample by adding 50 mL of bismuth nitrate solution through the air inlet tube after the air rate is set. Mix for 3 minutes prior to addition of  $\text{H}_2\text{SO}_4$  in step 6.

5. If samples are suspected to contain  $\text{NO}_3$  and/or  $\text{NO}_2$ , add 50 mL of sulfamic acid solution after the air rate is set through the air inlet tube. Mix for 3 min prior to addition of  $\text{H}_2\text{SO}_4$ .
6. Slowly add 50 mL 1:1  $\text{H}_2\text{SO}_4$  through the air inlet tube.
7. Rinse the tube with Type II water and allow the airflow to mix the flask contents for 3 min.
8. Pour 20 mL of magnesium chloride into the air inlet and wash down with stream of water.
9. Heat the solution to boiling. Reflux for 1 hr. Turn off heat and continue the airflow for at least 15 min. After cooling the boiling flask, disconnect absorber and close off the vacuum source.
10. Drain the solution from the absorber into a 250 mL volumetric flask. Wash the absorber with Type II water and add the washings to the flask. Dilute to the 250 mL with Type II water. The sample is now ready for analysis.

## 8.2 Aqueous Extraction

1. Weigh out a 25 g aliquot of the well-mixed sediment sample and quantitatively transfer the sediment to a wide-mouthed bottle containing 500 mL of ASTM Type II water.
2. Add 5 mL 50% sodium hydroxide solution and cap the bottle.

**NOTE:** The pH of the extract must be maintained above 10 throughout the extraction step and subsequent filtration. Since some sediment samples may be acidic, the pH must be monitored as follows: shake the extraction bottle and check the pH after one minute. If the pH is below 12, add 50% sodium hydroxide solution in 5 mL increments until it is at least 12. Recap the bottle and repeat this process until the pH does not drop.

3. Place the samples in a tumbler with enough foam insulation to cushion each bottle. Turn the tumbler on and allow the extraction to continue for approximately 16 hours.
4. Prepare the Buchner funnel apparatus with a glass fiber filter pad. Decant the extract to the Buchner funnel. Measure the volume of collected filtrate.

5. Place 500 mL of filtrate, or an aliquot diluted to 500 mL, in a 1 liter boiling flask.
6. Pipet 50 mL of 1.25 N sodium hydroxide solution into the absorbing tube of the reflux distillation apparatus. Connect the boiling flask, condenser, absorber, and trap in the train.
7. Adjust the vacuum source to allow a slow stream of air to enter the boiling flask. Approximately two bubbles of air per second should enter the boiling flask.
8. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper.

**NOTE:** If test is positive, treat the sample by adding 50 mL of bismuth nitrate solution through the air inlet tube after the air rate is set. Mix for 3 minutes prior to addition of  $\text{H}_2\text{SO}_4$  in step 6.

9. If samples are suspected to contain  $\text{NO}_3$  and/or  $\text{NO}_2$ , add 50 mL of sulfamic acid solution after the air rate is set through the air inlet tube. Mix for 3 min prior to addition of  $\text{H}_2\text{SO}_4$ .
10. Slowly add 50 mL 1:1  $\text{H}_2\text{SO}_4$  through the air inlet tube.
11. Rinse the tube with Type II water and allow the airflow to mix the flask contents for 3 min.
12. Pour 20 mL of magnesium chloride into the air inlet and wash down with stream of water.
13. Heat the solution to boiling. Reflux for 1 hr. Turn off heat and continue the airflow for at least 15 min. After cooling the boiling flask, disconnect absorber and close off the vacuum source.
14. Drain the solution from the absorber into a 250 mL volumetric flask. Wash the absorber with Type II water and add the washings to the flask. Dilute to the 250 mL with Type II water. The sample is now ready for analysis.

### 8.3 Automated Colorimetric Determination

1. Set up the manifold in a hood or a well-ventilated area.
2. Allow colorimeter and recorder to warm up for 30 min.
3. Run a baseline with all reagents feeding Type II water through the sample line.
4. Place appropriate standards in the sampler in order of decreasing concentration.
5. Complete loading of the sampler tray with unknown and quality assurance/quality control samples.

6. When the baseline becomes steady, begin the analysis.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for cyanide in sediments is 2000 µg/kg.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured cyanide concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the instrument detection limit.

### 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared

from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.6 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - cyanide, to the 100 mL aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The matrix spike should be prepared by adding cyanide from the working standard or intermediate cyanide standard to ensure a final concentration of approximately 40  $\mu\text{g/L}$ . The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have a relative percent difference (RPD) of  $\leq 20\%$ .

## 10.0 Method Performance

In a single laboratory study, recoveries of cyanide of 60 to 90% were reported for solid samples. The reported coefficients of variation were less than 13%.

## 11.0 Calculations and Reporting

The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences, such as those that contain sulfide (see section 11.1). The results of all other colorimetric analyses can be obtained by comparison of sample peak heights to the standard curve of peak heights of the standards plotted against their corresponding known concentration values.

### 11.1 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of

known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. Method 4500-CN C and 4500-CN E. 17th Edition, APHA, New York, New York. p. 4-29 - 4-31.

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

Goulden, P.D., B.K. Afghan, and P. Brooksbank. 1972. Determination of Nanogram Quantities of Simple and Complex Cyanides in Water. *Anal. Chem.* 44:1845-49.

U.S. EPA. 1986. *Test Methods for Evaluation of Solid Wastes*, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

# CYANIDE IN SEDIMENTS (COLORIMETRIC, MANUAL)

## 1.0 Scope and Application

This method is used to determine the concentration of inorganic cyanide in sediments. The method detects inorganic cyanides that may be present as either simple soluble salts or complex radicals.

The colorimetric method is sensitive to approximately 0.02 mg/L of cyanide in the final sediment distillate. The range of the procedure can be adjusted by modifying the sample preparation technique or the cell path length. However, the amount of sodium hydroxide in the standards and the sample to be analyzed must be the same.

This procedure is based on SW-846 Method 9010A (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

An aliquot of the sediment sample to be analyzed is placed in 500 mL of acidified distilled water. The resulting suspension is heated to distill hydrocyanic acid (HCN) from the acidic suspension and into a sodium hydroxide trap. The cyanide concentration of the final distillate is determined with a colorimetric procedure.

Cyanide in the distillate is reacted with chloramine-T at a pH less than 8 to produce cyanogen chloride (CNCl). After this reaction is complete, the addition of pyridine-barbituric acid reagent produces a red-blue color that is proportional to the cyanide concentration. The intensity of the color is measured by measuring sample absorbance at 578 nm. The concentration of NaOH must be the same in the standards, the sample distillate, and any dilutions of the original sample distillate to obtain colors of comparable intensity.

### 3.0 Interferences

Sulfides adversely affect the development of color in the analytical procedure. This interference can be reduced or eliminated by adding bismuth nitrate to the samples to precipitate the sulfide prior to distillation (Section 8.1.4). Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce sulfide during the distillation procedure should also be treated with bismuth nitrate prior to distillation.

Nitrate and/or nitrite in samples can act as a positive interference when present at concentrations above 10 mg/L and in the presence of certain organic compounds. These nitrogen compounds can form nitrous acid during the distillation process which will react with some organic compounds to form oxides. These oxides will decompose under conditions developed in the colorimetric procedure to generate HCN. This interference is eliminated by treating the samples with sulfamic acid prior to distillation (Section 8.1.5).

### 4.0 Apparatus and Materials

#### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Reflux distillation apparatus. The boiling flask should be of 1-liter size with inlet tube and provision for condenser. The gas absorber is a Fisher-Milligan scrubber (Fisher Catalog #07-513), or equivalent.
4. Spectrophotometer. Suitable for measurements at 578 nm with a 1.0 cm cell or larger.
5. Extractor. Any suitable device that sufficiently agitates a sealed container with a capacity of one liter or more. For the purpose of this procedure, agitation must be sufficient to: (1) maintain continuous contact between all sample particles and the extraction fluid, and (2) prevent stratification of the sample and the extraction fluid.
6. Buchner funnel, 500 mL capacity.
7. Vacuum filtration flask, 1 L.
8. Glass fiber filter pads.

9. Vacuum source, preferably a water driven aspirator. A valve or stopcock is needed to release the vacuum.
10. Top loading balance, capable of weighing 0.1 g.

## 4.2 Materials

1. Potassium iodide-starch test paper.
2. Volumetric flasks, class A, 250 mL.
3. Volumetric flasks, class A, 100 mL.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Bismuth nitrate solution ( $\text{Bi}(\text{NO}_3)_3$ ). Dissolve 30.0 grams of  $\text{Bi}(\text{NO}_3)_3$  in 100 mL of Type II water. While stirring, add 250 mL of glacial acetic acid. Stir until dissolved. Dilute to 1 liter with Type II water.
3. Chloramine-T solution. Dissolve 1.0 g of white, water-soluble, chloramine-T in 100 mL of Type II water. Refrigerate until ready to use.
4. Concentrated acetic acid ( $\text{C}_4\text{H}_6\text{O}_3$ ), glacial, reagent grade. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
5. Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ), reagent grade. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
6. Sulfuric acid (1:1). Slowly add 500 mL of concentrated  $\text{H}_2\text{SO}_4$  to 500 mL of Type II water.

**CAUTION:** This is an exothermic reaction.

7. Magnesium chloride solution ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ). Dissolve 510 g of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  into a 1 liter flask. Dilute to 1 liter with Type II water.
8. Pyridine-barbituric acid reagent. Place 15 g of barbituric acid ( $\text{C}_4\text{H}_4\text{O}_3\text{N}_2$ ) in a 250 mL volumetric flask. Add just enough Type II water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine ( $\text{C}_5\text{H}_5\text{N}$ ) and mix. Add 15 mL of concentrated HCl. Allow to cool to room temperature. Dilute to 250 mL with Type II water. This

reagent is stable for approximately six months, if stored in a cool, dark place.

9. Sodium dihydrogenphosphate ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ), 1 M. Dissolve 138 g of  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  in 1 liter of Type II water.
10. Sodium hydroxide solution (NaOH), 1.25 N. Dissolve 50 g of NaOH in Type II water. Dilute to 1 liter with Type II water.
11. Sodium hydroxide solution (NaOH), 50% (w/v). Dissolve 50 g of NaOH in 50 mL Type II water..
12. Sulfamic acid solution ( $\text{NH}_2\text{SO}_3\text{H}$ ). Dissolve 40 g of sulfamic acid in Type II water. Dilute to 1 liter with Type II water.
13. Cyanide stock solution. Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of Type II water. Standardize with 0.0192 N  $\text{AgNO}_3$ . Dilute to appropriate concentration of 1 mg/mL.
14. Intermediate standard cyanide solution. Dilute 100.0 mL of stock cyanide solution to 1 liter with Type II water (100  $\mu\text{g}/\text{mL}$  CN).
15. Working standard cyanide solution. Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1 liter with Type II water (10.0  $\mu\text{g}/\text{mL}$  CN). Store in a glass-stoppered bottle.

**NOTE:** All working standards should contain 2 mL of 1 N NaOH per 100 mL.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Since field-moist samples are used in the determination, preservation of the sample is not practical. Therefore, analysis should begin as soon as possible after sample collection. A holding time of 14 days is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of sediment samples to be analyzed for cyanide.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Two methods are given for preparing a standard cyanide curve. Section 7.1 should be followed if the samples do not contain sulfide and Section 7.2 should be followed if the samples to be analyzed contain sulfide. The difference between these two methods is that all the cyanide standards must be carried through the sample distillation process when sulfide is present.

### 7.1 Standard Curve for Samples without Sulfide.

1. Prepare a series of standards by pipetting suitable volumes of the working standard cyanide solution into 250 mL volumetric flasks. To each standard add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with Type II water. Prepare as follows:

<u>mL of Working Standard Solution</u> <u>(1 mL = 10 µg CN)</u>	<u>Concentration</u> <u>(µg CN/250 mL)</u>
0.0	BLANK
1.0	10
2.0	20
5.0	50
10.0	100
15.0	150
20.0	200

It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and a low) be distilled and compared with similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within  $\pm 10\%$  of the undistilled standards, the analyst should find the cause of the apparent error before proceeding.

2. Prepare a standard curve by plotting absorbances of standards vs. cyanide concentrations.

3. To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard cyanide solution or the working standard cyanide solution to 500 mL of sample to ensure a level of 20 µg/L. Proceed with the analysis as in Section 8.1 - Sample Distillation.

## 7.2 Standard Curve for Samples with Sulfide

1. All standards must be distilled in the same manner as the samples. A minimum of three standards shall be distilled.
2. Prepare a standard curve by plotting absorbance of standards vs. cyanide concentration.

## 8.0 Procedure

Two procedures are presented to isolate cyanide from the sediment matrix prior to analysis. The first is a direct distillation of the cyanide from a sediment-distilled water slurry (section 8.1) and the second is an aqueous extraction of cyanide from the sediment sample (section 8.2).

### 8.1 Sample Distillation

1. Weigh a 1 to 5 g aliquot of the homogenized field-moist sample and quantitatively transfer the sample to a 1 liter boiling flask containing 500 mL ASTM Type II water.
2. Pipet 50 mL of 1.25 N sodium hydroxide solution into the absorbing tube of the reflux distillation apparatus. Connect the boiling flask, condenser, absorber, and trap in the train.
3. Adjust the vacuum source to allow a slow stream of air to enter the boiling flask. Approximately two bubbles of air per second should enter the boiling flask.
4. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper.

**NOTE:** If test is positive, treat the sample by adding 50 mL of bismuth nitrate solution through the air inlet tube after the air rate is set. Mix for 3 minutes prior to addition of H<sub>2</sub>SO<sub>4</sub> in step 6.

5. If samples are suspected to contain  $\text{NO}_3$  and/or  $\text{NO}_2$ , add 50 mL of sulfamic acid solution after the air rate is set through the air inlet tube. Mix for 3 min prior to addition of  $\text{H}_2\text{SO}_4$ .
6. Slowly add 50 mL 1:1  $\text{H}_2\text{SO}_4$  through the air inlet tube.
7. Rinse the tube with Type II water and allow the airflow to mix the flask contents for 3 min.
8. Pour 20 mL of magnesium chloride into the air inlet and wash down with stream of water.
9. Heat the solution to boiling. Reflux for 1 hr. Turn off heat and continue the airflow for at least 15 min. After cooling the boiling flask, disconnect absorber and close off the vacuum source.
10. Drain the solution from the absorber into a 250 mL volumetric flask. Wash the absorber with Type II water and add the washings to the flask. Dilute to the 250 mL with Type II water. The sample is now ready for analysis.

## 8.2 Aqueous Extraction

1. Weigh out a 25 g aliquot of the well-mixed sediment sample and quantitatively transfer the sediment to a wide-mouthed bottle containing 500 mL of ASTM Type II water.
2. Add 5 mL 50% sodium hydroxide solution and cap the bottle.

**NOTE:** The pH of the extract must be maintained above 10 throughout the extraction step and subsequent filtration. Since some sediment samples may be acidic, the pH must be monitored as follows: shake the extraction bottle and check the pH after one minute. If the pH is below 12, add 50% sodium hydroxide solution in 5 mL increments until it is at least 12. Recap the bottle and repeat this process until the pH does not drop.

3. Place the samples in a tumbler with enough foam insulation to cushion each bottle. Turn the tumbler on and allow the extraction to continue for approximately 16 hours.
4. Prepare the Buchner funnel apparatus with a glass fiber filter pad. Decant the extract to the Buchner funnel. Measure the volume of collected filtrate.
5. Place 500 mL of filtrate, or an aliquot diluted to 500 mL, in a 1 liter boiling flask.

- Pipet 50 mL of 1.25 N sodium hydroxide solution into the absorbing tube of the reflux distillation apparatus. Connect the boiling flask, condenser, absorber, and trap in the train.
- Adjust the vacuum source to allow a slow stream of air to enter the boiling flask. Approximately two bubbles of air per second should enter the boiling flask.
- Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper.

**NOTE:** If test is positive, treat the sample by adding 50 mL of bismuth nitrate solution through the air inlet tube after the air rate is set. Mix for 3 minutes prior to addition of  $\text{H}_2\text{SO}_4$  in step 6.

- If samples are suspected to contain  $\text{NO}_3$  and/or  $\text{NO}_2$ , add 50 mL of sulfamic acid solution after the air rate is set through the air inlet tube. Mix for 3 min prior to addition of  $\text{H}_2\text{SO}_4$ .
- Slowly add 50 mL 1:1  $\text{H}_2\text{SO}_4$  through the air inlet tube.
- Rinse the tube with Type II water and allow the airflow to mix the flask contents for 3 min.
- Pour 20 mL of magnesium chloride into the air inlet and wash down with stream of water.
- Heat the solution to boiling. Reflux for 1 hr. Turn off heat and continue the airflow for at least 15 min. After cooling the boiling flask, disconnect absorber and close off the vacuum source.
- Drain the solution from the absorber into a 250 mL volumetric flask. Wash the absorber with Type II water and add the washings to the flask. Dilute to the 250 mL with Type II water. The sample is now ready for analysis.

### 8.3 Manual Spectrophotometric Analysis

- Withdraw 50 mL, or a smaller aliquot diluted to 50 mL with 1.25 N sodium hydroxide solution, of the final sample distillate and transfer to a 100 mL volumetric flask.
- Add 15.0 mL of sodium dihydrogenphosphate solution. Mix.
- Add 2 mL of Chloramine-T. Mix.

**NOTE:** Some distillates may contain compounds that have a chlorine demand. One minute after the addition of chloramine-T, test for residual chlorine with KI-starch paper. If the test is

negative, add an additional 0.5 mL chloramine-T. Recheck after 1 min.

**NOTE:** Temperature of reagents may affect the response factor of the colorimetric determination. The reagents stored under refrigerated conditions should be warmed to ambient temperature before use. Also, samples should not be left in a warm instrument to develop color but, instead, should be aliquoted to a cuvette immediately prior to reading the sample absorbance.

4. After 1 to 2 min, add 5 mL of pyridine-barbituric acid solution. Mix.
5. Dilute to 100 mL with Type II water. Mix.
6. Allow 8 min for color development and then read absorbance at 578 nm in a 1-cm cell within 15 min.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for cyanide in sediments is 2000 µg/kg.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured cyanide concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be ± 15% of the known value or within the certified value provided by the supplier, whichever is larger.

## 9.4 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the instrument detection limit.

## 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.6 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - cyanide, to the 100 mL aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The matrix spike should be prepared by adding cyanide from the working standard or intermediate cyanide standard to ensure a final concentration of approximately 40  $\mu\text{g/L}$ . The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 20\%$ .

## 10.0 Method Performance

In a single laboratory study, recoveries of cyanide of 60 to 90% were reported for solid samples. The reported coefficients of variation were less than 13%.

## 11.0 Calculations and Reporting

The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences, such as those that contain sulfide (see section 11.1). The results of all other colorimetric analyses can be obtained by

comparison of sample peak heights to the standard curve of peak heights of the standards plotted against their corresponding known concentration values.

## 11.1 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The

abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. Method 4500-CN C and 4500-CN E. 17th Edition, APHA, New York, New York. p. 4-29 - 4-31.

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

Goulden, P.D., B.K. Afghan, and P. Brooksbank. 1972. Determination of Nanogram Quantities of Simple and Complex Cyanides in Water. Anal. Chem. 44:1845-49.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

# ARSENIC IN SEDIMENTS

## 1.0 Scope and Application

This method is applicable to the determination of arsenic in sediment samples.

This procedure is based on EPA SW-846 Methods 3050 and 7060 (USEPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

An aliquot of the sediment sample is digested with nitric acid and hydrogen peroxide. Following dissolution, the digestate is spiked with a nickel nitrate solution and placed in a graphite furnace tube. The sample is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode or electrodeless discharge lamp (EDL) radiation during sample atomization is proportional to the arsenic concentration in the digestate.

## 3.0 Interferences

Elemental arsenic and many of its compounds are volatile; therefore, samples may be subject to potential loss of arsenic during the sample preparation procedure. Spiked samples and relevant standard reference materials should be processed to demonstrate the performance of the sample preparation technique.

Caution should also be employed when selecting the temperature and duration of the sample drying and charring (ashing) cycles. A nickel nitrate solution must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Simultaneous background correction must be employed to avoid

erroneously high results. Aluminum is a severe positive interferant in the analysis of arsenic, especially using D<sub>2</sub> arc background correction. Zeeman background correction is very useful in this situation.

If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected by means of blank burns, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, 3-5 weights covering expected weight range.
3. Drying oven, capable of maintaining 30° C.
4. Electric hot plate, adjustable and capable of maintaining a temperature of 90-95° C.
4. Thermometer, 0 to 100° C range.
5. Centrifuge and centrifuge tubes.
6. Atomic absorption spectrophotometer, single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip-chart recorder.
7. Arsenic hollow cathode lamp, or electrodeless discharge lamp (EDL). EDLs are recommended since they provide better sensitivity for arsenic analyses.
8. Graphite furnace. Any graphite furnace device with the appropriate temperature and timing controls.
9. Strip-chart recorder. A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, and changes in sensitivity can easily be recognized.

## 4.2 Materials

1. Conical Phillips beakers, 250 mL, or equivalent.
2. Watch glasses ribbed, or equivalent.
3. Volumetric flasks, class A, 10 mL.
4. Whatman no. 41 filter paper or equivalent.
5. Pipets. Microliter with disposable tips. Sizes can range from 5 to 1,000  $\mu\text{L}$ , as required.

## 5.0 Reagents and Standards

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated nitric acid, reagent grade ( $\text{HNO}_3$ ). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid is  $<\text{MDL}$ , then the acid can be used.
3. Hydrogen peroxide, 30% ( $\text{H}_2\text{O}_2$ ). Oxidant should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the  $\text{H}_2\text{O}_2$  is  $<\text{MDL}$ , then the acid can be used.
4. Arsenic standard stock solution (1,000 mg/L). Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide ( $\text{As}_2\text{O}_3$ , analytical reagent grade), or equivalent, in 100 mL of Type II water containing 4 g NaOH. Acidify the solution with 20 mL concentrated  $\text{HNO}_3$ . Dilute to 1 liter with Type II water (1 mL = 1 mg As).
5. Nickel nitrate solution, 5%. Dissolve 24.780 g of ACS reagent grade  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , or equivalent, in Type II water and dilute to 100 mL.
6. Nickel nitrate solution, 1%. Dilute 20 mL of the 5% nickel nitrate to 100 mL with Type II water.
7. Arsenic working standards. Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquot of the stock solution, add 1 mL of concentrated  $\text{HNO}_3$ , 2 mL of 30%  $\text{H}_2\text{O}_2$ , and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with Type II water.

## 6.0 Sample Handling and Preservation

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Since field-moist samples are used in the determination, preservation of the sample is not practical. Therefore, analysis should begin as soon as possible after sample collection. A holding time of 6 months is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of samples to be analyzed for arsenic in sediments.

Special containers (e.g., containers used for volatile organic analysis) may have to be used if the samples are to be analyzed for very volatile arsenic compounds.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^\circ \text{C}$ .

The oven or hot plate should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^\circ \text{C}$ .

Prepare a method blank and at least three standards in the appropriate concentration range to correlate arsenic concentrations with the atomic absorption spectrophotometer's linear response range. Prepare standards for instrument calibration by appropriate dilution of the stock arsenic solution. These standards should be prepared fresh on the day of use. Match the sample matrix and that of the standards as closely as possible.

Inject a suitable portion of each standard into the graphite furnace in order of increasing concentration. It is recommended that each standard solution be analyzed in triplicate in order to assess method precision. Instrument calibration curves should be composed of a minimum of a blank and three standards. A calibration curve should be prepared every day of continuous sample analysis and prior to the initiation of the project's routine sample analysis.

Construct an analytical curve by plotting the average peak absorbance or peak area for the standard solutions as a function of sample concentration on a linear graph. Prepare this graph daily when new initial calibration information is obtained. Alternatively, electronic instrument calibration can be used if the instrument is appropriately equipped.

## 8.0 Procedure

1. Weigh a 1.00 to 2.00 g aliquot of the homogenized, field-moist sediment to the nearest 0.01 g and quantitatively transfer the sample to a 250 mL beaker.
2. Add 10 mL 1:1 HNO<sub>3</sub>, mix the slurry, and cover the beaker opening with a watch glass.
3. Heat the sample to 95° C and reflux for 10 to 15 minutes without boiling.
4. Allow the sample to cool. Add 5 mL concentrated HNO<sub>3</sub>, replace the watch glass, and reflux for an additional 30 minutes.
5. Allow the sample to cool. Add 5 mL concentrated HNO<sub>3</sub> and cover the flask with a ribbed watch glass. Allow the solution to evaporate to a final volume of 5 mL without boiling while maintaining a covering of solution over the bottom of the beaker.
6. After the sample has cooled, add 2 mL Type II water and 3 mL H<sub>2</sub>O<sub>2</sub>. Cover the beaker with a watch glass and return the covered beaker to a hot plate or oven for warming and to initiate the peroxide reaction. Heat until the effervescence subsides. Allow the beaker to cool.

**NOTE:** Exercise care to ensure that sample is not lost due to excessively vigorous effervescence.

7. Continue to add 30% H<sub>2</sub>O<sub>2</sub> in 1 mL aliquots until the effervescence is minimal or until the general sample appearance is unchanged.

**NOTE:** The total volume of 30% H<sub>2</sub>O<sub>2</sub> added should not exceed 10 mL.

8. Cover the sample flask with a ribbed watch glass and continue heating until the volume of the acid-peroxide digestate has been reduced to approximately 5 mL. After cooling, dilute the final digestate to 100 mL with Type II water.
9. Suspended particulates should be removed by filtration, centrifugation, or by allowing the sample to settle prior to analysis.
  - a. Filtration. Filter digest through Whatman no. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.
  - b. Centrifugation. Centrifugation at 2,000 to 3,000 rpm for 10 minutes is usually sufficient to produce a clear supernatant.
10. Pipet 5 mL of the final sample digest into a 10-mL volumetric flask, add 1 mL of 1% nickel nitrate solution, and dilute to 10 mL with Type II water. The sample is now ready for injection into the furnace.
11. The 193.7-nm wavelength line and a background correction system are required. Follow the manufacturer's suggestions for all other spectrophotometer parameters.
12. Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.
13. Inject a measured microliter ( $\mu\text{L}$ ) aliquot of sample digest into the furnace and atomize. If the digest concentration is greater than the highest standard, or if the instrument response falls on the plateau of the calibration curve, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for arsenic in sediments is 1000 µg/kg (dry weight).

The detection limit specified in this method is presented to account for typical sediment background contents of chromium in the Great Lakes.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured arsenic concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards 2704 - Buffalo River sediment and 1646 - Estuarine sediment, should be run to monitor the life and performance of the graphite tube and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a routine sediment sample collected and homogenized in bulk that has undergone multiple analyses by the analytical laboratory. Alternately, a LCS can be created by spiking a known quantity of the contaminant(s) of concern into a clean sediment, homogenizing the bulk sample, followed by multiple analyses at the analytical laboratory. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

## 9.5 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the instrument detection limit.

## 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 15 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.7 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - arsenic, to a 1-2 g sample aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 3 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 20\%$ .

## 10.0 Method Performance

The optimal concentration range for this method is 5-100  $\mu\text{g/L}$ .

The data shown in Table 1 were obtained from records of state and contractor laboratories. The data provide an estimate of the precision that can be attained with the combined sample preparation and analysis method.

## 11.0 Calculations and Reporting

Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account.

Prepare a standard curve based on the absorbance and concentration of the arsenic standards. Determine the arsenic concentration in each of the sediment digests by comparing the digest absorbance with the standard curve.

Calculate the arsenic concentration of the sediment sample as follows:

$$\text{As, } \mu\text{g/kg (wet weight)} = \frac{X \times V \times 1000}{g}$$

$$\text{As, } \mu\text{g/kg (dry weight)} = \frac{X \times V \times 1000}{g \times \%S}$$

where:

X = is the arsenic concentration in the final sediment digest,  $\mu\text{g/L}$ .

V = the final sediment digest volume, 0.1 L.

g = the weight of wet sediment digested, g.

%S = the percent solids concentration of the field moist sediment sample expressed as a decimal fraction.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

Gaskill, A., 1986. Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Table 1. Method Performance Data (after Gaskill, 1986).

<u>Sample Matrix</u>	<u>Preparation Method</u>	<u>Laboratory Replicates</u>
Contaminated soil	3050	2.0, 1.8 µg/g
Oily soil	3050	3.3, 3.8 µg/g
NBS estuarine sediment (SRM 1646)	3050	8.1, 8.33 µg/g <sup>a</sup>
<u>Emission control dust</u>	<u>3050</u>	<u>430, 350 µg/g</u>

a = Bias of -30 and -28% from expected, respectively.

# CADMIUM IN SEDIMENTS (ICP)

## 1.0 Scope and Application

Inductively coupled plasma atomic emission spectroscopy (ICP) determines cadmium and numerous other elements that are present in solution. In order to apply this technique to sediments, the samples must be digested with nitric acid and hydrogen peroxide prior to analysis.

Detection limits, sensitivity, and optimum concentration ranges for cadmium, and other metals stable in a mixed standard solution with cadmium, will vary with the sample aliquot size, the spectrophotometer being used, and possible matrix interferences. Based on the estimated detection limit of 4 µg/L for cadmium in aqueous samples (Table 1), a sample size of 2 g, and a final digestate volume of 100 mL, the estimated detection limit for sediment samples is 200 µg/kg.

The method of standard addition (MSA) shall be used for the analysis of all sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required (see section 9).

This method should only be used by spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

This procedure is based on SW-846 Methods 3050 (for digestion) and 6010 for quantitation (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

A well-mixed, representative 1 to 2 g (wet weight) sample of sediment is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed using hydrochloric acid and diluted to volume.

**NOTE:** A separate sample shall be dried for a total solids determination in order to express the results on a dry-weight basis.

This instrumental method measures light emitted by cadmium in the final sediment digest by optical spectrometry. The digested samples are nebulized and the resulting aerosol is transported to a plasma torch. Cadmium-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes.

Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

The possibility of additional interferences named in section 3.0 should also be recognized and appropriate corrections made when necessary. The procedures that can be used for this purpose are described in section 9.

### 3.0 Interferences

Sediments represent diverse matrix types and samples from each location may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether the digestion procedure is appropriate for a specific sediment sample or there are matrix or other effects interfering with the analysis of the resultant sediment digestate.

#### 3.1 Spectral Interferences

Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multi-element instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferants can be assumed.

The magnitude of the interference effects summarized in Table 2 are expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that Cd is to be determined (at 226.502 nm) in a sample containing approximately 10 mg/L of Fe. According to Table 2, 100 mg/L of Fe would yield a false signal for Cd equivalent to approximately 0.03 mg/L. Therefore, the presence of 10 mg/L of Fe would result in a false signal for Cd equivalent to approximately 0.003 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, and argon flow rate.

The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

### 3.2 Physical Interferences

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Further, it has been reported that better control of the argon flow rate improves instrument performance. Improved argon flow rate control can be accomplished with the use of mass flow controllers.

### 3.3 Chemical Interferences

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, etc.), buffering of the sample, matrix matching, and standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Drying oven, capable of maintaining 30° C.
4. Thermometer, 0 to 200° C.
5. Centrifuge and centrifuge tubes.
6. Inductively coupled argon plasma emission spectrometer.
7. Computer-controlled emission spectrometer with background correction.
8. Radio frequency generator.
9. Argon gas supply, welding grade or better.

### 4.2 Materials

1. Conical Phillips beakers, 250 mL, or equivalent.
2. Watch glasses.
3. Whatman No. 41 filter paper, or equivalent.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.

3. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
4. Hydrogen peroxide, 30% (H<sub>2</sub>O<sub>2</sub>). Oxidant should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the H<sub>2</sub>O<sub>2</sub> is <MDL, then the acid can be used.
5. Nitric acid (1:1). Add 500 mL concentrated HNO<sub>3</sub> to 400 mL Type II water. Dilute to 1 liter with Type II water.
6. Hydrochloric acid (1:1). Add 500 mL concentrated HCl to 400 mL Type II water. Dilute to 1 liter with Type II water.
7. Standard stock solutions. May be purchased or prepared from ultrahigh purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hr at 105° C, unless otherwise specified.

**CAUTION:** Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

8. Beryllium standard stock solution (100 µg/mL). Dissolve 1.970 g BeSO<sub>4</sub>·4H<sub>2</sub>O (analytical reagent grade, undried), in 100 mL of Type II water, add 10.0 ml concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
9. Cadmium standard stock solution (100 µg/mL). Dissolve 0.1100 g CdO (analytical reagent grade) in a minimum amount of 1:1 HNO<sub>3</sub>. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
10. Lead standard stock solution (100 µg/mL). Dissolve 0.1600 g Pb(NO<sub>3</sub>)<sub>2</sub> (analytical reagent grade) in a minimum amount of 1:1 HNO<sub>3</sub>. Add 10 mL 1:1 HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
11. Manganese standard stock solution (100 µg/mL). Dissolve 0.1000 g of manganese metal, in an acid mixture of 10 mL concentrated HCl and 1 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
12. Selenium standard stock solution (100 µg/mL). Dissolve 0.1700 g H<sub>2</sub>SeO<sub>3</sub> (analytical reagent grade, undried) in 100 mL of Type II water. Dilute to 1 liter with Type II water.
13. Zinc standard stock solution (100 µg/mL). Dissolve 0.1200 g ZnO in a minimum amount of 1:1 HNO<sub>3</sub>. Add 10.0 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
14. Mixed calibration standard solutions. Care should be taken when preparing mixed standards for ICP analysis to ensure that the elements

in the final mixed standard are compatible and stable together. One set of mixed calibration standards that has been found to be useful is listed in Table 3. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities.

To prepare the mixed calibration standard for cadmium, combine appropriate volumes of the individual stock solutions indicated in Table 3 in volumetric flask. Add 2 mL 1:1 HNO<sub>3</sub> and 10 mL of 1:1 HCl and dilute to 100 mL with Type II water. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see section 9.9) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Si
IV	Al, Ca, Cr, K, Na, and Ni

**NOTE:** Premixed standard solutions (traceable to NIST) containing the combined elements as listed in solutions I through IV are available from a number of commercial vendors.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Since field-moist samples are used in the determination, preservation of the sample is not practical. Therefore, analysis should begin as soon as possible after sample collection. A holding time of 6 months is generally cited for this parameter. Samples may be stored for a longer period of time by air-drying or freezing. However, these samples should not be used for the preparation of sediment elutriates because the process of freezing and thawing the samples may influence the migration potential of sediment-associated constituents.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of samples to be analyzed for cadmium in sediments.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^\circ \text{C}$ .

The oven or hot plate should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^\circ \text{C}$ .

Prepare a calibration blank (see section 9.5.1) and at least three mixed calibration standards in the appropriate concentration range to correlate cadmium concentrations with the ICP's linear response range. Prepare standards for instrument calibration as instructed in section 5.14. Match the sample matrix and that of the standards as closely as possible.

Calibrate the instrument according to the instrument manufacturer's recommended procedures using typical mixed calibration standard solutions. Flush the system with the calibration blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

## 8.0 Procedure

### 8.1 Sample Digestion

1. Weigh a 1.00 to 2.00 g aliquot of the homogenized, field-moist sediment to the nearest 0.01 g and quantitatively transfer the sample to a 250 mL conical beaker.
2. Add 10 mL of 1:1 HNO<sub>3</sub>, mix the slurry, and cover with a watch glass.
3. Heat the sample to 95° C and reflux for 10 to 15 min without boiling.
4. Allow the sample to cool. Add 5 mL of concentrated HNO<sub>3</sub>, replace the watch glass, and reflux for 30 min. Repeat this last step to ensure complete oxidation of the sample. Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.
5. After the sample has cooled, add 2 mL of Type II water and 3 mL of 30% H<sub>2</sub>O<sub>2</sub>. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Heat until effervescence subsides. Allow the beaker to cool.

**NOTE:** Exercise care to ensure that sample is not lost due to excessively vigorous effervescence.

6. Continue to add 30% H<sub>2</sub>O<sub>2</sub> in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

**NOTE:** The total volume of the 30% H<sub>2</sub>O<sub>2</sub> should not exceed 10 mL.

7. Add 5 mL of concentrated HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and reflux for an additional 15 min without boiling. After cooling, dilute to 100 mL with Type II water.
8. Suspended particulates should be removed by filtration, by centrifugation, or by allowing the sample to settle prior to analysis.
  - a. Filtration: Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.
  - b. Centrifugation: Centrifugation at 2,000 to 3,000 rpm for 10 min is usually sufficient to clear the supernatant.

9. The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO<sub>3</sub>. The sample is now ready for analysis.

## 8.2 Sample Analysis

1. The analyst should follow the instructions provided by the instrument's manufacturer. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range where coordination factors are valid. The analyst must: (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.
2. Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this conditions.
3. Flush the system with the calibration blank solution for at least 1 min before the analysis of each sample. Analyze samples.

**NOTE:** Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for cadmium in sediments is 1000 µg/kg (dry weight).

The detection limit specified in this method is presented to account for typical sediment background contents of chromium in the Great Lakes.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured cadmium concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards 2704 - Buffalo River sediment and 1646 - Estuarine sediment, should be run to monitor performance of the ICP and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a routine sediment sample collected and homogenized in bulk that has undergone multiple analyses by the analytical laboratory. Alternately, a LCS can be created by spiking a known quantity of the contaminant(s) of concern into a clean sediment, homogenizing the bulk sample, followed by multiple analyses at the analytical laboratory. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

## 9.5 Blanks

Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

### 9.5.1 Calibration Blank

The calibration blank is prepared by diluting 2 mL of 1:1 HNO<sub>3</sub> and of 1:1 HCl to 100 mL with Type II water. Prepare a sufficient quantity to flush the system between standards and samples.

The calibration blank should be analyzed prior to routine sample analysis, after every 10 samples, and at the end of the analytical run. The measured concentration in the calibration blank should be less than or equal to the method detection limit.

### 9.5.2 Reagent Blank

The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.7 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - cadmium, to a 1-2 g sample aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have a relative percent difference (RPD) of  $\leq 20\%$ .

## 9.8 Interference Check Sample

The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the method detection limit for each element. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

The interference check sample should be analyzed at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Results should be within  $\pm 20\%$  of the known concentration.

## 9.9 Calibration Control Sample

A calibration control sample should be prepared in the same acid matrix as the calibration standards at 10 times the method detection limit. This sample should be prepared in accordance with the instructions provided by the supplier. The calibration control sample is used to verify the integrity of the calibration standards on a weekly basis.

## 9.10 Recommended Tests

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests will ensure the analyst that neither positive nor

negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

### 9.10.1 Serial Dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution should agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

### 9.10.2 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 10.0 Method Performance

In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was  $9 \pm 2\%$ . The mean percent recovery of spiked elements for all wastes was  $93 \pm 6\%$ . Spike levels ranged from 100  $\mu\text{g/L}$  to 100  $\text{mg/L}$ . The wastes included sludges and industrial wastewaters.

## 11.0 Calculations and Reporting

If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in  $\mu\text{g/kg}$  with up to three significant figures.

The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055. U.S. Environmental Protection Agency, Washington, D.C.

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Winge, R.K., V.J. Peterson, and V.A. Fassel. 1979. Inductively coupled plasma-atomic emission spectroscopy: Prominent lines, final report, March 1977 - February 1978, Ames laboratory, Ames, IA. EPA-600/4-79-017. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Table 1. Recommended Wavelengths and Estimated Instrumental Detection Limits.

Element	Wavelength <sup>a</sup> (nm)	Estimated Detection Limit <sup>b</sup> (µg/L)
Beryllium	313.042	0.3
Cadmium	226.502	4
Lead	220.353	42
Manganese	257.610	2
Selenium	196.026	75
Zinc	213.856	2

a - The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see section 3.1).

b - The estimated instrumental detection limits are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

Table 2. Analyte Concentration Equivalentents arising from Interference at the 100 mg/L Level.

Analyte	W (nm)	Interferant <sup>a,b</sup>									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Mi	Tl	V
Beryllium	313.042	-	-	-	-	-	-	-	-	0.04	0.05
Cadmium	226.502	-	-	-	-	0.03	-	-	0.02	-	-
Lead	220.353	0.17	-	-	-	-	-	-	-	-	-
Manganese	257.610	0.005	-	0.01	-	0.002	0.002	-	-	-	-
Selenium	196.026	0.23	-	-	-	0.09	-	-	-	-	-
Zinc	213.856	-	-	-	0.14	-	-	-	0.29	-	-

a - Dashes indicate that no interference was observed even when interferants were introduced at the following levels:

Al - 1000 mg/L,  
 Ca - 1000 mg/L,  
 Cr - 200 mg/L,  
 Cu - 200 mg/L,  
 Fe - 1000 mg/L,  
 Mg - 1000 mg/L,  
 Mn - 200 mg/L,  
 Tl - 200 mg/L,  
 V - 200 mg/L, and

b - The figures recorded as analyte concentrations are not the actual observed concentrations. To obtain those figures, add the listed concentration to the interferant figure.

Table 4. ICP Precision and Accuracy Data<sup>a</sup>

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
Cd	50	48	12	2.5	2.9	16	14	13	16
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se <sup>c</sup>	40	32	21.9	6	8.5	42	10	8.5	8.3

a - Not all elements were analyzed by all laboratories.

b - SD = standard deviation.

c - Results for Se are from two laboratories.

# CHROMIUM IN SEDIMENTS (ICP)

## 1.0 Scope and Application

Inductively coupled plasma atomic emission spectroscopy (ICP) determines chromium and numerous other elements that are present in solution. In order to apply this technique to sediments, the samples must be digested with nitric acid and hydrogen peroxide prior to analysis.

Detection limits, sensitivity, and optimum concentration ranges for chromium, and other metals stable in a mixed standard solution with chromium, will vary with the sample aliquot size, the spectrophotometer being used, and possible matrix interferences. Based on the estimated detection limit of 7 µg/L for chromium in aqueous samples (Table 1), a sample size of 2 g, and a final digestate volume of 100 mL, the estimated detection limit for sediment samples is 350 µg/kg.

The method of standard addition (MSA) shall be used for the analysis of all sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required (see section 9).

This method should only be used by spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

This procedure is based on SW-846 Methods 3050 (for digestion) and 6010 for quantitation (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

A well-mixed, representative 1 to 2 g (wet weight) sample of sediment is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed using hydrochloric acid and diluted to volume.

**NOTE:** A separate sample shall be dried for a total solids determination in order to express the results on a dry-weight basis.

This instrumental method measures light emitted by chromium in the final sediment digest by optical spectrometry. The digested samples are nebulized and the resulting aerosol is transported to a plasma torch. Chromium-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes.

Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

The possibility of additional interferences named in section 3.0 should also be recognized and appropriate corrections made when necessary. The procedures that can be used for this purpose are described in section 9.

### 3.0 Interferences

Sediments represent diverse matrix types and samples from each location may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether the digestion procedure is appropriate for a specific sediment sample or there are matrix or other effects interfering with the analysis of the resultant sediment digestate.

#### 3.1 Spectral Interferences

Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multi-element instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferants can be assumed.

The magnitude of the interference effects summarized in Table 2 are expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that Cd is to be determined (at 267.716 nm) in a sample containing approximately 10 mg/L of Mn. According to Table 2, 100 mg/L of Mn would yield a false signal for Cr equivalent to approximately 0.04 mg/L. Therefore, the presence of 10 mg/L of Mn would result in a false signal for Cr equivalent to approximately 0.004 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, and argon flow rate.

The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

### 3.2 Physical Interferences

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Further, it has been reported that better control of the argon flow rate improves instrument performance. Improved argon flow rate control can be accomplished with the use of mass flow controllers.

### 3.3 Chemical Interferences

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, etc.), buffering of the sample, matrix matching, and standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Drying oven, capable of maintaining 30° C.
4. Thermometer, 0 to 200° C.
5. Centrifuge and centrifuge tubes.
6. Inductively coupled argon plasma emission spectrometer.
7. Computer-controlled emission spectrometer with background correction.
8. Radio frequency generator.
9. Argon gas supply, welding grade or better.

### 4.2 Materials

1. Conical Phillips beakers, 250 mL, or equivalent.
2. Watch glasses.
3. Whatman No. 41 filter paper, or equivalent.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.

3. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
4. Hydrogen peroxide, 30% (H<sub>2</sub>O<sub>2</sub>). Oxidant should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the H<sub>2</sub>O<sub>2</sub> is <MDL, then the acid can be used.
5. Nitric acid (1:1). Add 500 mL concentrated HNO<sub>3</sub> to 400 mL Type II water. Dilute to 1 liter with Type II water.
6. Hydrochloric acid (1:1). Add 500 mL concentrated HCl to 400 mL Type II water. Dilute to 1 liter with Type II water.
7. Standard stock solutions. May be purchased or prepared from ultrahigh purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hr at 105° C, unless otherwise specified.

**CAUTION:** Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

8. Aluminum standard stock solution (100 µg/mL). Dissolve 0.1000 g of aluminum metal in an acid mixture of 4 mL of 1:1 HCl and 1 mL of concentrated HNO<sub>3</sub> in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of 1:1 HCl. Dilute to 1 liter with Type II water.
9. Calcium standard stock solution (100 µg/mL). Suspend 0.2500 g CaCO<sub>3</sub> dried at 180° C for 1 hr before weighing in Type II water and dissolve cautiously with a minimum amount of 1:1 HNO<sub>3</sub>. Add 10.0 mL of concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
10. Chromium standard stock solution (100 µg/mL). Dissolve 0.1900 g CrO<sub>3</sub> in Type II water. When solution is complete, acidify with 10 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
11. Potassium standard stock solution (100 µg/mL). Dissolve 0.1900 g KCl dried at 110° C in Type II water. Dilute to 1 liter with Type II water.
12. Sodium standard stock solution (100 µg/mL). Dissolve 0.2500 g NaCl in Type II water. Add 10.0 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
13. Nickel standard stock solution (100 µg/mL). Dissolve 0.1000 g of nickel metal in 10.0 mL hot concentrated HNO<sub>3</sub>. Cool. Dilute to 1 liter with Type II water.
14. Mixed calibration standard solutions. Care should be taken when preparing mixed standards for ICP analysis to ensure that the elements

in the final mixed standard are compatible and stable together. One set of mixed calibration standards that has been found to be useful is listed in Table 3. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities.

To prepare the mixed calibration standard for chromium, combine appropriate volumes of the individual stock solutions indicated in Table 3 in volumetric flask. Add 2 mL 1:1 HNO<sub>3</sub> and 10 mL of 1:1 HCl and dilute to 100 mL with Type II water. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see section 9.9) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Si
IV	Al, Ca, Cr, K, Na, and Ni

**NOTE:** Premixed standard solutions (traceable to NIST) containing the combined elements as listed in solutions I through IV are available from a number of commercial vendors.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Since field-moist samples are used in the determination, preservation of the sample is not practical. Therefore, analysis should begin as soon as possible after sample collection. A holding time of 6 months is generally cited for this parameter. Samples may be stored for a longer period of time by air-drying or freezing. However, these samples should not be used for the preparation of sediment elutriates because the process of freezing and thawing the samples may influence the migration potential of sediment-associated constituents.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of samples to be analyzed for chromium in sediments.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^\circ \text{C}$ .

The oven or hot plate should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^\circ \text{C}$ .

Prepare a calibration blank (see section 9.5.1) and at least three mixed calibration standards in the appropriate concentration range to correlate chromium concentrations with the ICP's linear response range. Prepare standards for instrument calibration as instructed in section 5.14. Match the sample matrix and that of the standards as closely as possible.

Calibrate the instrument according to the instrument manufacturer's recommended procedures using typical mixed calibration standard solutions. Flush the system with the calibration blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

## 8.0 Procedure

### 8.1 Sample Digestion

1. Weigh a 1.00 to 2.00 g aliquot of the homogenized, field-moist sediment to the nearest 0.01 g and quantitatively transfer the sample to a 250 mL conical beaker.
2. Add 10 mL of 1:1 HNO<sub>3</sub>, mix the slurry, and cover with a watch glass.
3. Heat the sample to 95° C and reflux for 10 to 15 min without boiling.
4. Allow the sample to cool. Add 5 mL of concentrated HNO<sub>3</sub>, replace the watch glass, and reflux for 30 min. Repeat this last step to ensure complete oxidation of the sample. Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.
5. After the sample has cooled, add 2 mL of Type II water and 3 mL of 30% H<sub>2</sub>O<sub>2</sub>. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Heat until effervescence subsides. Allow the beaker to cool.

**NOTE:** Exercise care to ensure that sample is not lost due to excessively vigorous effervescence.

6. Continue to add 30% H<sub>2</sub>O<sub>2</sub> in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

**NOTE:** The total volume of the 30% H<sub>2</sub>O<sub>2</sub> should not exceed 10 mL.

7. Add 5 mL of concentrated HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and reflux for an additional 15 min without boiling. After cooling, dilute to 100 mL with Type II water.
8. Suspended particulates should be removed by filtration, by centrifugation, or by allowing the sample to settle prior to analysis.
  - a. Filtration: Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.
  - b. Centrifugation: Centrifugation at 2,000 to 3,000 rpm for 10 min is usually sufficient to clear the supernatant.

9. The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO<sub>3</sub>. The sample is now ready for analysis.

## 8.2 Sample Analysis

1. The analyst should follow the instructions provided by the instrument's manufacturer. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range where coordination factors are valid. The analyst must: (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.
2. Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this conditions.
3. Flush the system with the calibration blank solution for at least 1 min before the analysis of each sample. Analyze samples.

**NOTE:** Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for chromium in sediments is 20 mg/kg (dry weight).

The detection limit specified in this method is presented to account for typical sediment background contents of chromium in the Great Lakes.

## 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured arsenic concentrations.

## 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards 2704 - Buffalo River sediment and 1646 - Estuarine sediment, should be run to monitor the performance of the ICP and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

## 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a routine sediment sample collected and homogenized in bulk that has undergone multiple analyses by the analytical laboratory. Alternately, a LCS can be created by spiking a known quantity of the contaminant(s) of concern into a clean sediment, homogenizing the bulk sample, followed by multiple analyses at the analytical laboratory. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

## 9.5 Blanks

Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

### 9.5.1 Calibration Blank

The calibration blank is prepared by diluting 2 mL of 1:1 HNO<sub>3</sub> and of 1:1 HCl to 100 mL with Type II water. Prepare a sufficient quantity to flush the system between standards and samples.

The calibration blank should be analyzed prior to routine sample analysis, after every 10 samples, and at the end of the analytical run. The measured concentration in the calibration blank should be less than or equal to the method detection limit.

### 9.5.2 Reagent Blank

The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.7 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - chromium, to a 1-2 g sample aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and

analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 20\%$ .

## 9.8 Interference Check Sample

The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the method detection limit for each element. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

The interference check sample should be analyzed at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Results should be within  $\pm 20\%$  of the known concentration.

## 9.9 Calibration Control Sample

A calibration control sample should be prepared in the same acid matrix as the calibration standards at 10 times the method detection limit. This sample should be prepared in accordance with the instructions provided by the supplier. The calibration control sample is used to verify the integrity of the calibration standards on a weekly basis.

## 9.10 Recommended Tests

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

### 9.10.1 Serial Dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution

should agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

### 9.10.2 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The

abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 10.0 Method Performance

In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was  $9 \pm 2\%$ . The mean percent recovery of spiked elements for all wastes was  $93 \pm 6\%$ . Spike levels ranged from 100  $\mu\text{g/L}$  to 100  $\text{mg/L}$ . The wastes included sludges and industrial wastewaters.

## 11.0 Calculations and Reporting

If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in  $\mu\text{g/kg}$  with up to three significant figures.

The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Winge, R.K., V.J. Peterson, and V.A. Fassel. 1979. Inductively coupled plasma-atomic emission spectroscopy: Prominent lines, final report, March 1977 -

February 1978, Ames laboratory, Ames, IA. EPA-600/4-79-017. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Table 1. Recommended Wavelengths and Estimated Instrumental Detection Limits.

Element	Wavelength <sup>a</sup> (nm)	Estimated Detection Limit <sup>b</sup> (µg/L)
Aluminum	308.215	45
Chromium	267.716	7
Copper	324.754	6
Nickel	231.604	15
Potassium	766.491	See footnote c
Sodium	588.995	29

a - The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see section 3.1).

b - The estimated instrumental detection limits are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

c - Highly dependent on operating conditions and plasma position.

Table 2. Analyte Concentration Equivalents arising from Interference at the 100 mg/L Level.

Analyte	Wavelength (nm)	Interferant <sup>a,b</sup>									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Mo	Tl	V
Aluminum	308.215	-	-	-	-	-	-	0.21	-	-	1.4
Calcium	317.933	-	-	0.08	-	0.01	0.01	0.04	-	0.03	0.03
Chromium	267.716	-	-	-	-	0.003	-	0.04	-	-	0.04
Nickel	231.604	-	-	-	-	-	-	-	-	-	-
Sodium	588.995	0.30	-	-	-	-	-	-	-	-	-

a - Dashes indicate that no interference was observed even when interferants were introduced at the following levels:

Al - 1000 mg/L,  
 Ca - 1000 mg/L,  
 Cr - 200 mg/L,  
 Cu - 200 mg/L,  
 Fe - 1000 mg/L,  
 Mg - 1000 mg/L,  
 Mn - 200 mg/L,  
 Tl - 200 mg/L,  
 V - 200 mg/L, and

b - The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

Table 4. ICP Precision and Accuracy Data<sup>a</sup>

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)
Cr	150	149	3.8	10	10	18	50	50	3.3
Al	700	695	5.6	60	62	33	160	161	13
Ni	250	245	5.8	30	28	11	60	55	14

a - Not all elements were analyzed by all laboratories.

b - SD = standard deviation.

# COPPER IN SEDIMENTS (ICP)

## 1.0 Scope and Application

Inductively coupled plasma atomic emission spectroscopy (ICP) determines copper and numerous other elements that are present in solution. In order to apply this technique to sediments, the samples must be digested with nitric acid and hydrogen peroxide prior to analysis.

Detection limits, sensitivity, and optimum concentration ranges for copper, and other metals stable in a mixed standard solution with copper, will vary with the sample aliquot size, the spectrophotometer being used, and possible matrix interferences. Based on the estimated detection limit of 6 µg/L for copper in aqueous samples (Table 1), a sample size of 2 g, and a final digestate volume of 100 mL, the estimated detection limit for sediment samples is 300 µg/kg.

The method of standard addition (MSA) shall be used for the analysis of all sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required (see section 9).

This method should only be used by spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

This procedure is based on SW-846 Methods 3050 (for digestion) and 6010 for quantitation (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

A well-mixed, representative 1 to 2 g (wet weight) sample of sediment is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed using hydrochloric acid and diluted to volume.

**NOTE:** A separate sample shall be dried for a total solids determination in order to express the results on a dry-weight basis.

This instrumental method measures light emitted by copper in the final sediment digest by optical spectrometry. The digested samples are nebulized and the resulting aerosol is transported to a plasma torch. Copper-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes.

Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

The possibility of additional interferences named in section 3.0 should also be recognized and appropriate corrections made when necessary. The procedures that can be used for this purpose are described in section 9.

### 3.0 Interferences

Sediments represent diverse matrix types and samples from each location may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether the digestion procedure is appropriate for a specific sediment sample or there are matrix or other effects interfering with the analysis of the resultant sediment digestate.

#### 3.1 Spectral Interferences

Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multi-element instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferants can be assumed.

The magnitude of the interference effects summarized in Table 2 are expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that Cu is to be determined (at 324.754 nm) in a sample containing approximately 10 mg/L of V. According to Table 2, 100 mg/L of V would yield a false signal for Cu equivalent to approximately 0.02 mg/L. Therefore, the presence of 10 mg/L of V would result in a false signal for Cu equivalent to approximately 0.002 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, and argon flow rate.

The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

### 3.2 Physical Interferences

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Further, it has been reported that better control of the argon flow rate improves instrument performance. Improved argon flow rate control can be accomplished with the use of mass flow controllers.

### 3.3 Chemical Interferences

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, etc.), buffering of the sample, matrix matching, and standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Drying oven, capable of maintaining 30° C.
4. Thermometer, 0 to 200° C.
5. Centrifuge and centrifuge tubes.
6. Inductively coupled argon plasma emission spectrometer.
7. Computer-controlled emission spectrometer with background correction.
8. Radio frequency generator.
9. Argon gas supply, welding grade or better.

### 4.2 Materials

1. Conical Phillips beakers, 250 mL, or equivalent.
2. Watch glasses.
3. Whatman No. 41 filter paper, or equivalent.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.

3. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
4. Hydrogen peroxide, 30% (H<sub>2</sub>O<sub>2</sub>). Oxidant should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the H<sub>2</sub>O<sub>2</sub> is <MDL, then the acid can be used.
5. Nitric acid (1:1). Add 500 mL concentrated HNO<sub>3</sub> to 400 mL Type II water. Dilute to 1 liter with Type II water.
6. Hydrochloric acid (1:1). Add 500 mL concentrated HCl to 400 mL Type II water. Dilute to 1 liter with Type II water.
7. Standard stock solutions. May be purchased or prepared from ultrahigh purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hr at 105° C, unless otherwise specified.

**CAUTION:** Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

8. Barium standard stock solution (100 µg/mL). Dissolve 0.1500 g BaCl<sub>2</sub> dried at 250° C for 2 hr in 10 mL Type II water with 1 mL 1:1 HCl. Add 10.0 mL 1:1 HCl. Dilute to 1 liter with Type II water.
9. Cobalt standard stock solution (100 µg/mL). Dissolve 0.1000 g of cobalt metal in a minimum amount of 1:1 HNO<sub>3</sub>. Add 10.0 mL 1:1 HCl. Dilute to 1 liter with Type II water.
10. Copper standard stock solution (100 µg/mL). Dissolve 0.1300 g CuO in a minimum amount of 1:1 HNO<sub>3</sub>. Add 10.0 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
11. Iron standard stock solution (100 µg/mL). Dissolve 0.1400 g Fe<sub>2</sub>O<sub>3</sub> in a warm mixture of 20 mL 1:1 HCl and 2 mL of concentrated HNO<sub>3</sub>. Cool. Add an additional 5.0 mL of concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
12. Vanadium standard stock solution (100 µg/mL). Dissolve 0.2300 g NH<sub>4</sub>VO<sub>3</sub> in a minimum amount of concentrated HNO<sub>3</sub>. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
13. Mixed calibration standard solutions. Care should be taken when preparing mixed standards for ICP analysis to ensure that the elements in the final mixed standard are compatible and stable together. One set of mixed calibration standards that has been found to be useful is listed in Table 3. Prior to preparing the mixed standards, each stock solution

should be analyzed separately to determine possible spectral interferences or the presence of impurities.

To prepare the mixed calibration standard for copper, combine appropriate volumes of the individual stock solutions indicated in Table 3 in volumetric flask. Add 2 mL 1:1 HNO<sub>3</sub> and 10 mL of 1:1 HCl and dilute to 100 mL with Type II water. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see section 9.9) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Si
IV	Al, Ca, Cr, K, Na, and Ni

**NOTE:** Premixed standard solutions (traceable to NIST) containing the combined elements as listed in solutions I through IV are available from a number of commercial vendors.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Since field-moist samples are used in the determination, preservation of the sample is not practical. Therefore, analysis should begin as soon as possible after sample collection. A holding time of 6 months is generally cited for this parameter.

Samples may be stored for a longer period of time by air-drying or freezing. However, these samples should not be used for the preparation of sediment elutriates because the process of freezing and thawing the samples may influence the migration potential of sediment-associated constituents.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of samples to be analyzed for copper in sediments.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^{\circ}$  C.

The oven or hot plate should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^{\circ}$  C.

Prepare a calibration blank (see section 9.5.1) and at least three mixed calibration standards in the appropriate concentration range to correlate copper concentrations with the ICP's linear response range. Prepare standards for instrument calibration as instructed in section 5.13. Match the sample matrix and that of the standards as closely as possible.

Calibrate the instrument according to the instrument manufacturer's recommended procedures using typical mixed calibration standard solutions. Flush the system with the calibration blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

## 8.0 Procedure

### 8.1 Sample Digestion

1. Weigh a 1.00 to 2.00 g aliquot of the homogenized, field-moist sediment to the nearest 0.01 g and quantitatively transfer the sample to a 250 mL conical beaker.
2. Add 10 mL of 1:1 HNO<sub>3</sub>, mix the slurry, and cover with a watch glass.
3. Heat the sample to 95° C and reflux for 10 to 15 min without boiling.
4. Allow the sample to cool. Add 5 mL of concentrated HNO<sub>3</sub>, replace the watch glass, and reflux for 30 min. Repeat this last step to ensure complete oxidation of the sample. Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.
5. After the sample has cooled, add 2 mL of Type II water and 3 mL of 30% H<sub>2</sub>O<sub>2</sub>. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Heat until effervescence subsides. Allow the beaker to cool.

**NOTE:** Exercise care to ensure that sample is not lost due to excessively vigorous effervescence.

6. Continue to add 30% H<sub>2</sub>O<sub>2</sub> in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

**NOTE:** The total volume of the 30% H<sub>2</sub>O<sub>2</sub> should not exceed 10 mL.

7. Add 5 mL of concentrated HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and reflux for an additional 15 min without boiling. After cooling, dilute to 100 mL with Type II water.
8. Suspended particulates should be removed by filtration, by centrifugation, or by allowing the sample to settle prior to analysis.
  - a. Filtration: Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.
  - b. Centrifugation: Centrifugation at 2,000 to 3,000 rpm for 10 min is usually sufficient to clear the supernatant.

9. The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO<sub>3</sub>. The sample is now ready for analysis.

## 8.2 Sample Analysis

1. The analyst should follow the instructions provided by the instrument's manufacturer. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range where coordination factors are valid. The analyst must: (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.
2. Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this conditions.
3. Flush the system with the calibration blank solution for at least 1 min before the analysis of each sample. Analyze samples.

**NOTE:** Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for copper in sediments is 5 mg/kg (dry weight).

The detection limit specified in this method is presented to account for typical sediment background contents of chromium in the Great Lakes.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured arsenic concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards 2704 - Buffalo River sediment and 1646 - Estuarine sediment, should be run to monitor the performance of the ICP and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a routine sediment sample collected and homogenized in bulk that has undergone multiple analyses by the analytical laboratory. Alternately, a LCS can be created by spiking a known quantity of the contaminant(s) of concern into a clean sediment, homogenizing the bulk sample, followed by multiple analyses at the analytical laboratory. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

## 9.5 Blanks

Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

### 9.5.1 Calibration Blank

The calibration blank is prepared by diluting 2 mL of 1:1 HNO<sub>3</sub> and of 1:1 HCl to 100 mL with Type II water. Prepare a sufficient quantity to flush the system between standards and samples.

The calibration blank should be analyzed prior to routine sample analysis, after every 10 samples, and at the end of the analytical run. The measured concentration in the calibration blank should be less than or equal to the method detection limit.

### 9.5.2 Reagent Blank

The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.7 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - copper, to a 1-2 g sample aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have a relative percent difference (RPD) of  $\leq 20\%$ .

## 9.8 Interference Check Sample

The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the method detection limit for each element. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

The interference check sample should be analyzed at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Results should be within  $\pm 20\%$  of the known concentration.

## 9.9 Calibration Control Sample

A calibration control sample should be prepared in the same acid matrix as the calibration standards at 10 times the method detection limit. This sample should be prepared in accordance with the instructions provided by the supplier. The calibration control sample is used to verify the integrity of the calibration standards on a weekly basis.

## 9.10 Recommended Tests

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests will ensure the analyst that neither positive nor

negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

### 9.10.1 Serial Dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution should agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

### 9.10.2 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 10.0 Method Performance

In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was  $9 \pm 2\%$ . The mean percent recovery of spiked elements for all wastes was  $93 \pm 6\%$ . Spike levels ranged from 100  $\mu\text{g/L}$  to 100  $\text{mg/L}$ . The wastes included sludges and industrial wastewaters.

## 11.0 Calculations and Reporting

If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in  $\mu\text{g/kg}$  with up to three significant figures.

The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Winge, R.K., V.J. Peterson, and V.A. Fassel. 1979. Inductively coupled plasma-atomic emission spectroscopy: Prominent lines, final report, March 1977 - February 1978, Ames laboratory, Ames, IA. EPA-600/4-79-017. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Table 1. Recommended Wavelengths and Estimated Instrumental Detection Limits.

Element	Wavelength <sup>a</sup> (nm)	Estimated Detection Limit <sup>b</sup> (µg/L)
Barium	455.403	2
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Vanadium	292.402	8

a - The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see section 3.1).

b - The estimated instrumental detection limits are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

Table 2. Analyte Concentration Equivalents arising from Interference at the 100 mg/L Level.

Analyte	Wavelength (nm)	Interferant <sup>a,b</sup>									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Mo	Tl	V
Barium	455.403	-	-	-	-	-	-	-	-	-	-
Cobalt	228.616	-	-	0.03	-	0.005	-	-	0.03	0.15	-
Copper	324.754	-	-	-	-	0.003	-	-	-	0.05	0.02
Iron	259.940	-	-	-	-	-	-	0.12	-	-	-
Vanadium	292.402	-	-	0.05	-	0.005	-	-	-	0.02	-

a - Dashes indicate that no interference was observed even when interferants were introduced at the following levels:

Al - 1000 mg/L,  
 Ca - 1000 mg/L,  
 Cr - 200 mg/L,  
 Cu - 200 mg/L,  
 Fe - 1000 mg/L,  
 Mg - 1000 mg/L,  
 Mn - 200 mg/L,  
 Tl - 200 mg/L,  
 V - 200 mg/L, and

b - The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

Table 4. ICP Precision and Accuracy Data<sup>a</sup>

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)
V	750	749	1.8	70	69	2.9	170	169	1.1
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Co	700	512	10	20	20	4.1	120	108	21

a - Not all elements were analyzed by all laboratories.

b - SD = standard deviation.

# MERCURY IN SEDIMENTS (MANUAL CVAA)

## 1.0 Scope and Application

This method is appropriate for the determination of mercury in sediment samples. All samples must be subjected to acid dissolution prior to analysis.

This procedure is based on SW-846 Method 7471 (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

An aliquot of the sediment sample is digested with aqua regia at elevated temperatures. The resultant solution is then treated with potassium permanganate to reduce any mercury that is present to the elemental state.

The sample is attached to a cold vapor atomic absorption apparatus and the elemental mercury is flushed from the sample in a stream of air. The mercury vapor is passed through a cell positioned in the light path of an atomic absorption spectrophotometer. The mercury concentration in the sample is proportional to the absorption of incident radiation with a wavelength of 253.7 nm.

## 3.0 Interferences

Potassium permanganate is added during the sample preparation step to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from ASTM Type II water.

Although copper has also been reported to interfere with the analysis of mercury, studies suggest that copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

Interference from certain volatile organic materials, which may absorb radiation at a wavelength of 253 nm, is also possible but seldom encountered

(EPA, 1979). A preliminary run without reagents can be performed to identify the presence of and to correct for this matrix effect.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, 3-5 weights covering expected weight range.
3. Electric hot plate, adjustable and capable of maintaining a temperature of 90-95° C.
4. Thermometer, 0 to 100° C range.
5. Atomic absorption spectrophotometer. Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.
6. Mercury hollow cathode lamp or electrodeless discharge lamp.
7. Recorder. Any multi-range variable-speed recorder that is compatible with the UV detection system is suitable.
8. Absorption cell. Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 2.54 cm O.D. x 11.43 cm. The ends are ground perpendicular to the longitudinal axis, and quartz windows (2.54 cm diameter x 0.16 cm thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 5.08 cm x 5.08 cm cards. Holes with a diameter of 2.54 cm are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.
9. Air pump. Any peristaltic pump capable of delivering 1 L/min air may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.
10. Flowmeter. Capable of measuring an air flow of 1 L/min.

11. Aeration tube. A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.
12. Drying tube, 15.2 cm X 1.90 cm diameter tube containing 20 g of magnesium perchlorate.

**NOTE:** In place of the magnesium perchlorate drying tube, a small reading lamp with a 60 W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10° C above ambient.

13. Cold vapor generator.
  - a. The apparatus shown in Figure 1 is a closed system. An open system, in which the mercury vapor is passed through the absorption cell only once, may be used in place of the closed system.
  - b. Because mercury vapor is potentially toxic, precautions must be taken to avoid inhalation of the vapor. Therefore, a bypass has been included in the analytical apparatus to either vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium such as:
    1. equal volumes of 0.1 M  $\text{KMnO}_4$  and 10%  $\text{H}_2\text{SO}_4$ ,
    2. 0.25% iodine in a 3% KI solution, or
    3. specially treated charcoal that will absorb mercury vapor.

## 4.2 Materials

1. BOD bottles, 300 mL, or equivalent.
2. Aluminum foil.
3. Volumetric flasks, class A, 100 mL.
4. Graduated cylinders, various sizes up to 100 mL, or equivalent.

## 5.0 Reagents and Standards

1. ASTM Type II water (ASTM D1193). Water supply should be continually tested to verify that contaminants are not present at levels that will interfere with method performance.

2. Hydrochloric acid (HCl), conc. reagent grade.
3. Nitric acid (HNO<sub>3</sub>), conc. reagent grade.
4. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), conc. reagent grade.
5. Aqua regia. Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO<sub>3</sub>.
6. Sulfuric acid, 0.5 N. Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter with ASTM Type II water.
7. Stannous sulfate. Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use.

**NOTE:** Stannous chloride may be used in place of stannous sulfate.

8. Sodium chloride-hydroxylamine sulfate solution. Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in ASTM Type II water. Dilute to 100 mL with Type II water.

**NOTE:** Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

9. Potassium permanganate, 5% w/v solution (KMnO<sub>4</sub>). Dissolve 5 g of potassium permanganate in 100 mL of ASTM Type II water.
10. Mercury stock solution. Dissolve 0.1354 g of mercuric chloride in 75 mL of ASTM Type II water. Add 10 mL of concentrated nitric acid and adjust the volume to 100 mL with ASTM Type II water. (1.0 mL = 1.0 mg Hg).
11. Mercury working solution. Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 µg/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding mercury stock solution.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Since field-moist samples are used in the determination, preservation of the sample is not practical. Therefore, analysis should begin as soon as possible after sample collection. A holding time of 28 days is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of samples to be analyzed for arsenic in sediments.

If sediment samples are to be dried prior to analysis, moisture should be driven off at a temperature of 60° C or less to minimize the potential volatilization of mercury.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^\circ \text{C}$ .

The hot plate/water bath should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^\circ \text{C}$ .

Calibration curves should be composed of a minimum of a blank and three standards. To calibrate and standardize to atomic absorption spectrophotometer, the following steps should be used to prepare standards and prepare the instrument:

1. Transfer 0.0, 0.5, 1.0, 2.0, 5.0, and 10-mL aliquots of the mercury working standard containing 0-1.0  $\mu\text{g}$ , respectively, of mercury to a series of 300-mL BOD bottles.
2. Add enough ASTM Type II water to each bottle to make a total volume of 10 mL.
3. Add 5 mL of aqua regia and heat 2 min in a water bath at 95° C.
4. Allow the sample to cool.

5. Add 50 mL ASTM Type II water and 15 mL of  $\text{KMnO}_4$  solution to each bottle and return to the water bath for 30 min.
6. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate.
7. Add 50 mL of ASTM Type II water.
8. To the first standard, add 5 mL of stannous sulfate solution, and immediately attach the bottle to the aeration apparatus. At this point, the sample is allowed to stand quietly without manual agitation.
9. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to a minimum value. Due to the potential toxicity of these vapors, they should be properly vented through a fume hood or absorbing medium.
10. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue the aeration.
11. Repeat steps 8 through 10 for each of the standards.
12. Construct a standard curve by plotting the recorded absorbance versus the concentration of mercury in the standards.

## 8.0 Procedure

### 8.1 Sample Digestion

Digest and oxidize the sediment sample using the procedure specified in either step 8.1.1 or 8.1.2.

#### 8.1.1 Sample Digestion Option 1 - Water Bath Digestion

1. Weigh a 0.2 to 0.5 g aliquot of well mixed, field-moist sediment sample and transfer to the bottom of a BOD bottle.
2. Add 5 mL of ASTM Type II water and 5 mL of aqua regia.
3. Heat 2 min in a water bath at  $95^\circ \text{C}$  and allow to cool.
4. Add 50 mL ASTM Type II water and 15 mL potassium permanganate solution to each sample bottle.
5. Mix thoroughly and place in the water bath for 30 min at  $95^\circ \text{C}$ .

6. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

**CAUTION:** Do this addition under a vacuum hood since  $\text{Cl}_2$  could be evolved.

7. Add 55 mL of ASTM Type II water.
8. Continue as described in step 8.2.

### 8.1.2 Sample Digestion Option 2 - Autoclave Digestion

1. Weigh a 0.2 g aliquot of well mixed, field-moist sediment sample and transfer to the bottom of a BOD bottle.
2. Add 5 mL of concentrated  $\text{H}_2\text{SO}_4$  and 2 mL of concentrated  $\text{HNO}_3$ .
3. Add 5 mL of saturated  $\text{KMnO}_4$  solution and cover the bottle with a piece of aluminum foil.
4. Autoclave samples at  $121^\circ \text{C}$  and 15 psi for 15 minutes and allow to cool.
5. Add 50 mL ASTM Type II water and 15 mL potassium permanganate solution to each sample bottle.
6. Cool and bring the volume of the sample to 100 mL with ASTM Type II water.
7. Add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

**CAUTION:** Do this addition under a vacuum hood as  $\text{Cl}_2$  could be evolved.

8. Purge the dead air space and continue as described in step 8.2.

## 8.2 Sample Analysis

1. To the first sample, add 5 mL of stannous sulfate solution, and immediately attach the bottle to the aeration apparatus. At this point, the sample is allowed to stand quietly without manual agitation.
2. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to a minimum

- value. Due to the potential toxicity of these vapors, they should be properly vented through a fume hood or absorbing medium.
3. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue the aeration.
  4. Repeat steps 1 through 3 for each of the samples.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for mercury in sediments is 0.002 mg/kg (dry weight).

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured arsenic concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards 2704 - Buffalo River sediment and 1646 - Estuarine sediment, should be run to monitor the life and performance of the graphite tube and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a routine sediment sample collected and homogenized in bulk that has undergone multiple analyses by the analytical laboratory. Alternately, a LCS can be created by spiking a known quantity of the contaminant(s) of concern into a clean sediment, homogenizing the

bulk sample, followed by multiple analyses at the analytical laboratory. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

## 9.5 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the instrument detection limit.

## 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 15 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.7 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - arsenic, to a 1-2 g sample aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 3 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have a relative percent difference (RPD) of  $\leq 20\%$ .

Samples with a concentration above the highest standard or an absorbance that fall on the plateau of the calibration curve should be diluted and reanalyzed.

## 10.0 Method Performance

The general range of this method with sediment samples, which is dependent upon sample size, is 0.2 to 5  $\mu\text{g/g}$  (EPA, 1979).

The analysis of replicate sediment samples using the digestion procedure in step 8.1.1 and the cold vapor analytical technique produced the following standard deviations at the indicated levels:

$$0.29 \mu\text{g/g} \pm 0.02, \text{ and} \\ 0.82 \mu\text{g/g} \pm 0.03.$$

Recoveries of mercury at these levels, added as methyl mercuric chloride, were 97% and 94%, respectively.

The data shown in Table 1 were obtained from records of state and contractor laboratories. The data provide an estimate of the precision that can be attained with the combined sample preparation and analysis method.

## 11.0 Calculations and Reporting

Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5  $\mu\text{g/g}$  dry weight).

Measure the peak height or absorbance of the sample from the chart and determine the mercury concentration from the standard curve.

Calculate the mercury concentration in the sediment sample using the following calculation:

$$\text{Hg, } \mu\text{g/kg (dry weight)} = \frac{X \times V}{g \times \%S}$$

where:

- X = is the mercury concentration in the final sediment digest,  $\mu\text{g/L}$ .
- V = the final sediment digest volume, L.
- g = the weight of wet sediment digested, g.
- %S = the percent solids concentration of the field moist sediment sample expressed as a decimal fraction.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

Gaskill, A., 1986. Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075.

U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Table 1. Method Performance Data (after Gaskill, 1986).

<u>Sample Matrix</u>	<u>Preparation Method</u>	<u>Laboratory Replicates</u>
Emission control dust	unknown	12, 12 µg/g
<u>Wastewater treatment sludge</u>	<u>unknown</u>	<u>0., 0.28 µg/g</u>

# NICKEL IN SEDIMENTS (ICP)

## 1.0 Scope and Application

Inductively coupled plasma atomic emission spectroscopy (ICP) determines nickel and numerous other elements that are present in solution. In order to apply this technique to sediments, the samples must be digested with nitric acid and hydrogen peroxide prior to analysis.

Detection limits, sensitivity, and optimum concentration ranges for nickel, and other metals stable in a mixed standard solution with nickel, will vary with the sample aliquot size, the spectrophotometer being used, and possible matrix interferences. Based on the estimated detection limit of 15 µg/L for nickel in aqueous samples (Table 1), a sample size of 2 g, and a final digestate volume of 100 mL, the estimated detection limit for sediment samples is 750 µg/kg.

The method of standard addition (MSA) shall be used for the analysis of all sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required (see section 9).

This method should only be used by spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

This procedure is based on SW-846 Methods 3050 (for digestion) and 6010 for quantitation (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

A well-mixed, representative 1 to 2 g (wet weight) sample of sediment is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed using hydrochloric acid and diluted to volume.

**NOTE:** A separate sample shall be dried for a total solids determination in order to express the results on a dry-weight basis.

This instrumental method measures light emitted by nickel in the final sediment digest by optical spectrometry. The digested samples are nebulized and the resulting aerosol is transported to a plasma torch. Nickel-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes.

Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

The possibility of additional interferences named in section 3.0 should also be recognized and appropriate corrections made when necessary. The procedures that can be used for this purpose are described in section 9.

### 3.0 Interferences

Sediments represent diverse matrix types and samples from each location may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether the digestion procedure is appropriate for a specific sediment sample or there are matrix or other effects interfering with the analysis of the resultant sediment digestate.

#### 3.1 Spectral Interferences

Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multi-element instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferants can be assumed.

The magnitude of the interference effects summarized in Table 2 are expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, and argon flow rate.

The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

### 3.2 Physical Interferences

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Further, it has been reported that better control of the argon flow rate improves instrument performance. Improved argon flow rate control can be accomplished with the use of mass flow controllers.

### 3.3 Chemical Interferences

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant

with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, etc.), buffering of the sample, matrix matching, and standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Drying oven, capable of maintaining 30° C.
4. Thermometer, 0 to 200° C.
5. Centrifuge and centrifuge tubes.
6. Inductively coupled argon plasma emission spectrometer.
7. Computer-controlled emission spectrometer with background correction.
8. Radio frequency generator.
9. Argon gas supply, welding grade or better.

### 4.2 Materials

1. Conical Phillips beakers, 250 mL, or equivalent.
2. Watch glasses.
3. Whatman No. 41 filter paper, or equivalent.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
3. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.

4. Hydrogen peroxide, 30% (H<sub>2</sub>O<sub>2</sub>). Oxidant should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the H<sub>2</sub>O<sub>2</sub> is <MDL, then the acid can be used.
5. Nitric acid (1:1). Add 500 mL concentrated HNO<sub>3</sub> to 400 mL Type II water. Dilute to 1 liter with Type II water.
6. Hydrochloric acid (1:1). Add 500 mL concentrated HCl to 400 mL Type II water. Dilute to 1 liter with Type II water.
7. Standard stock solutions. May be purchased or prepared from ultrahigh purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hr at 105° C, unless otherwise specified.

**CAUTION:** Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

8. Aluminum standard stock solution (100 µg/mL). Dissolve 0.1000 g of aluminum metal in an acid mixture of 4 mL of 1:1 HCl and 1 mL of concentrated HNO<sub>3</sub> in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of 1:1 HCl. Dilute to 1 liter with Type II water.
9. Calcium standard stock solution (100 µg/mL). Suspend 0.2500 g CaCO<sub>3</sub> dried at 180° C for 1 hr before weighing in Type II water and dissolve cautiously with a minimum amount of 1:1 HNO<sub>3</sub>. Add 10.0 mL of concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
10. Chromium standard stock solution (100 µg/mL). Dissolve 0.1900 g CrO<sub>3</sub> in Type II water. When solution is complete, acidify with 10 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
11. Potassium standard stock solution (100 µg/mL). Dissolve 0.1900 g KCl dried at 110° C in Type II water. Dilute to 1 liter with Type II water.
12. Sodium standard stock solution (100 µg/mL). Dissolve 0.2500 g NaCl in Type II water. Add 10.0 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
13. Nickel standard stock solution (100 µg/mL). Dissolve 0.1000 g of nickel metal in 10.0 mL hot concentrated HNO<sub>3</sub>. Cool. Dilute to 1 liter with Type II water.
14. Mixed calibration standard solutions. Care should be taken when preparing mixed standards for ICP analysis to ensure that the elements in the final mixed standard are compatible and stable together. One set of mixed calibration standards that has been found to be useful is listed in Table 3. Prior to preparing the mixed standards, each stock solution

should be analyzed separately to determine possible spectral interferences or the presence of impurities.

To prepare the mixed calibration standard for nickel, combine appropriate volumes of the individual stock solutions indicated in Table 3 in volumetric flask. Add 2 mL 1:1 HNO<sub>3</sub> and 10 mL of 1:1 HCl and dilute to 100 mL with Type II water. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see section 9.9) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Si
IV	Al, Ca, Cr, K, Na, and Ni

**NOTE:** Premixed standard solutions (traceable to NIST) containing the combined elements as listed in solutions I through IV are available from a number of commercial vendors.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Since field-moist samples are used in the determination, preservation of the sample is not practical. Therefore, analysis should begin as soon as possible after sample collection. A holding time of 6 months is generally cited for this parameter.

Samples may be stored for a longer period of time by air-drying or freezing. However, these samples should not be used for the preparation of sediment elutriates because the process of freezing and thawing the samples may influence the migration potential of sediment-associated constituents.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of samples to be analyzed for nickel in sediments.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^{\circ}$  C.

The oven or hot plate should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^{\circ}$  C.

Prepare a calibration blank (see section 9.5.1) and at least three mixed calibration standards in the appropriate concentration range to correlate nickel concentrations with the ICP's linear response range. Prepare standards for instrument calibration as instructed in section 5.14. Match the sample matrix and that of the standards as closely as possible.

Calibrate the instrument according to the instrument manufacturer's recommended procedures using typical mixed calibration standard solutions. Flush the system with the calibration blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

## 8.0 Procedure

### 8.1 Sample Digestion

1. Weigh a 1.00 to 2.00 g aliquot of the homogenized, field-moist sediment to the nearest 0.01 g and quantitatively transfer the sample to a 250 mL conical beaker.
2. Add 10 mL of 1:1 HNO<sub>3</sub>, mix the slurry, and cover with a watch glass.
3. Heat the sample to 95° C and reflux for 10 to 15 min without boiling.
4. Allow the sample to cool. Add 5 mL of concentrated HNO<sub>3</sub>, replace the watch glass, and reflux for 30 min. Repeat this last step to ensure complete oxidation of the sample. Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.
5. After the sample has cooled, add 2 mL of Type II water and 3 mL of 30% H<sub>2</sub>O<sub>2</sub>. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Heat until effervescence subsides. Allow the beaker to cool.

**NOTE:** Exercise care to ensure that sample is not lost due to excessively vigorous effervescence.

6. Continue to add 30% H<sub>2</sub>O<sub>2</sub> in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

**NOTE:** The total volume of the 30% H<sub>2</sub>O<sub>2</sub> should not exceed 10 mL.

7. Add 5 mL of concentrated HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and reflux for an additional 15 min without boiling. After cooling, dilute to 100 mL with Type II water.
8. Suspended particulates should be removed by filtration, by centrifugation, or by allowing the sample to settle prior to analysis.
  - a. Filtration: Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.
  - b. Centrifugation: Centrifugation at 2,000 to 3,000 rpm for 10 min is usually sufficient to clear the supernatant.

9. The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO<sub>3</sub>. The sample is now ready for analysis.

## 8.2 Sample Analysis

1. The analyst should follow the instructions provided by the instrument's manufacturer. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range where coordination factors are valid. The analyst must: (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.
2. Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this conditions.
3. Flush the system with the calibration blank solution for at least 1 min before the analysis of each sample. Analyze samples.

**NOTE:** Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for nickel in sediments is 15 mg/kg (dry weight).

The detection limit specified in this method is presented to account for typical sediment background contents of chromium in the Great Lakes.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured arsenic concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards 2704 - Buffalo River sediment and 1646 - Estuarine sediment, should be run to monitor the performance of the ICP and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a routine sediment sample collected and homogenized in bulk that has undergone multiple analyses by the analytical laboratory. Alternately, a LCS can be created by spiking a known quantity of the contaminant(s) of concern into a clean sediment, homogenizing the bulk sample, followed by multiple analyses at the analytical laboratory. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

## 9.5 Blanks

Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

### 9.5.1 Calibration Blank

The calibration blank is prepared by diluting 2 mL of 1:1 HNO<sub>3</sub> and of 1:1 HCl to 100 mL with Type II water. Prepare a sufficient quantity to flush the system between standards and samples.

The calibration blank should be analyzed prior to routine sample analysis, after every 10 samples, and at the end of the analytical run. The measured concentration in the calibration blank should be less than or equal to the method detection limit.

### 9.5.2 Reagent Blank

The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.7 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - nickel, to a 1-2 g sample aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have a relative percent difference (RPD) of  $\leq 20\%$ .

## 9.8 Interference Check Sample

The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the method detection limit for each element. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

The interference check sample should be analyzed at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Results should be within  $\pm 20\%$  of the known concentration.

## 9.9 Calibration Control Sample

A calibration control sample should be prepared in the same acid matrix as the calibration standards at 10 times the method detection limit. This sample should be prepared in accordance with the instructions provided by the supplier. The calibration control sample is used to verify the integrity of the calibration standards on a weekly basis.

## 9.10 Recommended Tests

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests will ensure the analyst that neither positive nor

negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

### 9.10.1 Serial Dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution should agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

### 9.10.2 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 10.0 Method Performance

In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was  $9 \pm 2\%$ . The mean percent recovery of spiked elements for all wastes was  $93 \pm 6\%$ . Spike levels ranged from 100  $\mu\text{g/L}$  to 100  $\text{mg/L}$ . The wastes included sludges and industrial wastewaters.

## 11.0 Calculations and Reporting

If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in  $\mu\text{g/kg}$  with up to three significant figures.

The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Winge, R.K., V.J. Peterson, and V.A. Fassel. 1979. Inductively coupled plasma-atomic emission spectroscopy: Prominent lines, final report, March 1977 - February 1978, Ames laboratory, Ames, IA. EPA-600/4-79-017. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Table 1. Recommended Wavelengths and Estimated Instrumental Detection Limits.

Element	Wavelength <sup>a</sup> (nm)	Estimated Detection Limit <sup>b</sup> (µg/L)
Aluminum	308.215	45
Chromium	267.716	7
Copper	324.754	6
Nickel	231.604	15
Potassium	766.491	See footnote c
Sodium	588.995	29

a - The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see section 3.1).

b - The estimated instrumental detection limits are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

c - Highly dependent on operating conditions and plasma position.

Table 2. Analyte Concentration Equivalentents arising from Interference at the 100 mg/L Level.

Analyte	Wavelength (nm)	Interferant <sup>a,b</sup>									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Mo	Tl	V
Aluminum	308.215	-	-	-	-	-	-	0.21	-	-	1.4
Calcium	317.933	-	-	0.08	-	0.01	0.01	0.04	-	0.03	0.03
Chromium	267.716	-	-	-	-	0.003	-	0.04	-	-	0.04
Nickel	231.604	-	-	-	-	-	-	-	-	-	-
Sodium	588.995	0.30	-	-	-	-	-	-	-	-	-

a - Dashes indicate that no interference was observed even when interferants were introduced at the following levels:

Al - 1000 mg/L,  
 Ca - 1000 mg/L,  
 Cr - 200 mg/L,  
 Cu - 200 mg/L,  
 Fe - 1000 mg/L,  
 Mg - 1000 mg/L,  
 Mn - 200 mg/L,  
 Tl - 200 mg/L,  
 V - 200 mg/L, and

b - The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

Table 4. ICP Precision and Accuracy Data<sup>a</sup>

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)
Cr	150	149	3.8	10	10	18	50	50	3.3
Al	700	695	5.6	60	62	33	160	161	13
Ni	250	245	5.8	30	28	11	60	55	14

a - Not all elements were analyzed by all laboratories.

b - SD = standard deviation.

# LEAD IN SEDIMENTS (ICP)

## 1.0 Scope and Application

Inductively coupled plasma atomic emission spectroscopy (ICP) determines lead and numerous other elements that are present in solution. In order to apply this technique to sediments, the samples must be digested with nitric acid and hydrogen peroxide prior to analysis.

Detection limits, sensitivity, and optimum concentration ranges for lead, and other metals stable in a mixed standard solution with lead, will vary with the sample aliquot size, the spectrophotometer being used, and possible matrix interferences. Based on the estimated detection limit of 42 µg/L for lead in aqueous samples (Table 1), a sample size of 2 g, and a final digestate volume of 100 mL, the estimated detection limit for sediment samples is 2100 µg/kg.

The method of standard addition (MSA) shall be used for the analysis of all sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required (see section 9).

This method should only be used by spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

This procedure is based on SW-846 Methods 3050 (for digestion) and 6010 for quantitation (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

A well-mixed, representative 1 to 2 g (wet weight) sample of sediment is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed using hydrochloric acid and diluted to volume.

**NOTE:** A separate sample shall be dried for a total solids determination in order to express the results on a dry-weight basis.

This instrumental method measures light emitted by lead in the final sediment digest by optical spectrometry. The digested samples are nebulized and the resulting aerosol is transported to a plasma torch. Lead-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes.

Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

The possibility of additional interferences named in section 3.0 should also be recognized and appropriate corrections made when necessary. The procedures that can be used for this purpose are described in section 9.

### 3.0 Interferences

Sediments represent diverse matrix types and samples from each location may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether the digestion procedure is appropriate for a specific sediment sample or there are matrix or other effects interfering with the analysis of the resultant sediment digestate.

#### 3.1 Spectral Interferences

Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multi-element instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferants can be assumed.

The magnitude of the interference effects summarized in Table 2 are expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that Pb is to be determined (at 220.353 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for Pb equivalent to approximately 0.17 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for Pb equivalent to approximately 0.017 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, and argon flow rate.

The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

### 3.2 Physical Interferences

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Further, it has been reported that better control of the argon flow rate improves instrument performance. Improved argon flow rate control can be accomplished with the use of mass flow controllers.

### 3.3 Chemical Interferences

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, etc.), buffering of the sample, matrix matching, and standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Drying oven, capable of maintaining 30° C.
4. Thermometer, 0 to 200° C.
5. Centrifuge and centrifuge tubes.
6. Inductively coupled argon plasma emission spectrometer.
7. Computer-controlled emission spectrometer with background correction.
8. Radio frequency generator.
9. Argon gas supply, welding grade or better.

### 4.2 Materials

1. Conical Phillips beakers, 250 mL, or equivalent.
2. Watch glasses.
3. Whatman No. 41 filter paper, or equivalent.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.

3. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
4. Hydrogen peroxide, 30% (H<sub>2</sub>O<sub>2</sub>). Oxidant should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the H<sub>2</sub>O<sub>2</sub> is <MDL, then the acid can be used.
5. Nitric acid (1:1). Add 500 mL concentrated HNO<sub>3</sub> to 400 mL Type II water. Dilute to 1 liter with Type II water.
6. Hydrochloric acid (1:1). Add 500 mL concentrated HCl to 400 mL Type II water. Dilute to 1 liter with Type II water.
7. Standard stock solutions. May be purchased or prepared from ultrahigh purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hr at 105° C, unless otherwise specified.

**CAUTION:** Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

8. Beryllium standard stock solution (100 µg/mL). Dissolve 1.970 g BeSO<sub>4</sub>·4H<sub>2</sub>O (analytical reagent grade, undried), in 100 mL of Type II water, add 10.0 ml concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
9. Cadmium standard stock solution (100 µg/mL). Dissolve 0.1100 g CdO (analytical reagent grade) in a minimum amount of 1:1 HNO<sub>3</sub>. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
10. Lead standard stock solution (100 µg/mL). Dissolve 0.1600 g Pb(NO<sub>3</sub>)<sub>2</sub> (analytical reagent grade) in a minimum amount of 1:1 HNO<sub>3</sub>. Add 10 mL 1:1 HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
11. Manganese standard stock solution (100 µg/mL). Dissolve 0.1000 g of manganese metal, in an acid mixture of 10 mL concentrated HCl and 1 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
12. Selenium standard stock solution (100 µg/mL). Dissolve 0.1700 g H<sub>2</sub>SeO<sub>3</sub> (analytical reagent grade, undried) in 100 mL of Type II water. Dilute to 1 liter with Type II water.
13. Zinc standard stock solution (100 µg/mL). Dissolve 0.1200 g ZnO in a minimum amount of 1:1 HNO<sub>3</sub>. Add 10.0 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
14. Mixed calibration standard solutions. Care should be taken when preparing mixed standards for ICP analysis to ensure that the elements

in the final mixed standard are compatible and stable together. One set of mixed calibration standards that has been found to be useful is listed in Table 3. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities.

To prepare the mixed calibration standard for lead, combine appropriate volumes of the individual stock solutions indicated in Table 3 in volumetric flask. Add 2 mL 1:1 HNO<sub>3</sub> and 10 mL of 1:1 HCl and dilute to 100 mL with Type II water. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see section 9.9) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Si
IV	Al, Ca, Cr, K, Na, and Ni

**NOTE:** Premixed standard solutions (traceable to NIST) containing the combined elements as listed in solutions I through IV are available from a number of commercial vendors.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Since field-moist samples are used in the determination, preservation of the sample is not practical. Therefore, analysis should begin as soon as possible after sample collection. A holding time of 6 months is generally cited for this parameter. Samples may be stored for a longer period of time by air-drying or freezing. However, these samples should not be used for the preparation of sediment elutriates because the process of freezing and thawing the samples may influence the migration potential of sediment-associated constituents.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of samples to be analyzed for lead in sediments.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^\circ \text{C}$ .

The oven or hot plate should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^\circ \text{C}$ .

Prepare a calibration blank (see section 9.5.1) and at least three mixed calibration standards in the appropriate concentration range to correlate lead concentrations with the ICP's linear response range. Prepare standards for instrument calibration as instructed in section 5.14. Match the sample matrix and that of the standards as closely as possible.

Calibrate the instrument according to the instrument manufacturer's recommended procedures using typical mixed calibration standard solutions. Flush the system with the calibration blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

## 8.0 Procedure

### 8.1 Sample Digestion

1. Weigh a 1.00 to 2.00 g aliquot of the homogenized, field-moist sediment to the nearest 0.01 g and quantitatively transfer the sample to a 250 mL conical beaker.
2. Add 10 mL of 1:1 HNO<sub>3</sub>, mix the slurry, and cover with a watch glass.
3. Heat the sample to 95° C and reflux for 10 to 15 min without boiling.
4. Allow the sample to cool. Add 5 mL of concentrated HNO<sub>3</sub>, replace the watch glass, and reflux for 30 min. Repeat this last step to ensure complete oxidation of the sample. Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.
5. After the sample has cooled, add 2 mL of Type II water and 3 mL of 30% H<sub>2</sub>O<sub>2</sub>. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Heat until effervescence subsides. Allow the beaker to cool.

**NOTE:** Exercise care to ensure that sample is not lost due to excessively vigorous effervescence.

6. Continue to add 30% H<sub>2</sub>O<sub>2</sub> in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

**NOTE:** The total volume of the 30% H<sub>2</sub>O<sub>2</sub> should not exceed 10 mL.

7. Add 5 mL of concentrated HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and reflux for an additional 15 min without boiling. After cooling, dilute to 100 mL with Type II water.
8. Suspended particulates should be removed by filtration, by centrifugation, or by allowing the sample to settle prior to analysis.
  - a. Filtration: Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.
  - b. Centrifugation: Centrifugation at 2,000 to 3,000 rpm for 10 min is usually sufficient to clear the supernatant.

9. The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO<sub>3</sub>. The sample is now ready for analysis.

## 8.2 Sample Analysis

1. The analyst should follow the instructions provided by the instrument's manufacturer. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range where coordination factors are valid. The analyst must: (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.
2. Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this conditions.
3. Flush the system with the calibration blank solution for at least 1 min before the analysis of each sample. Analyze samples.

**NOTE:** Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for lead in sediments is 10 mg/kg (dry weight).

The detection limit specified in this method is presented to account for typical sediment background contents of chromium in the Great Lakes.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured arsenic concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards 2704 - Buffalo River sediment and 1646 - Estuarine sediment, should be run to monitor the performance of the ICP and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a routine sediment sample collected and homogenized in bulk that has undergone multiple analyses by the analytical laboratory. Alternately, a LCS can be created by spiking a known quantity of the contaminant(s) of concern into a clean sediment, homogenizing the bulk sample, followed by multiple analyses at the analytical laboratory. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

## 9.5 Blanks

Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

### 9.5.1 Calibration Blank

The calibration blank is prepared by diluting 2 mL of 1:1 HNO<sub>3</sub> and of 1:1 HCl to 100 mL with Type II water. Prepare a sufficient quantity to flush the system between standards and samples.

The calibration blank should be analyzed prior to routine sample analysis, after every 10 samples, and at the end of the analytical run. The measured concentration in the calibration blank should be less than or equal to the method detection limit.

### 9.5.2 Reagent Blank

The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.7 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - lead, to a 1-2 g sample aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have a relative percent difference (RPD) of  $\leq 20\%$ .

## 9.8 Interference Check Sample

The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the method detection limit for each element. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

The interference check sample should be analyzed at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Results should be within  $\pm 20\%$  of the known concentration.

## 9.9 Calibration Control Sample

A calibration control sample should be prepared in the same acid matrix as the calibration standards at 10 times the method detection limit. This sample should be prepared in accordance with the instructions provided by the supplier. The calibration control sample is used to verify the integrity of the calibration standards on a weekly basis.

## 9.10 Recommended Tests

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests will ensure the analyst that neither positive nor

negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

### 9.10.1 Serial Dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution should agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

### 9.10.2 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 10.0 Method Performance

In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was  $9 \pm 2\%$ . The mean percent recovery of spiked elements for all wastes was  $93 \pm 6\%$ . Spike levels ranged from 100  $\mu\text{g/L}$  to 100  $\text{mg/L}$ . The wastes included sludges and industrial wastewaters.

## 11.0 Calculations and Reporting

If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in  $\mu\text{g/kg}$  with up to three significant figures.

The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Winge, R.K., V.J. Peterson, and V.A. Fassel. 1979. Inductively coupled plasma-atomic emission spectroscopy: Prominent lines, final report, March 1977 - February 1978, Ames laboratory, Ames, IA. EPA-600/4-79-017. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Table 1. Recommended Wavelengths and Estimated Instrumental Detection Limits.

Element	Wavelength <sup>a</sup> (nm)	Estimated Detection Limit <sup>b</sup> (µg/L)
Beryllium	313.042	0.3
Cadmium	226.502	4
Lead	220.353	42
Manganese	257.610	2
Selenium	196.026	75
Zinc	213.856	2

a - The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see section 3.1).

b - The estimated instrumental detection limits are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

Table 2. Analyte Concentration Equivalentents arising from Interference at the 100 mg/L Level.

Analyte	Wavelength (nm)	Interferant <sup>a,b</sup>									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Mi	Tl	V
Beryllium	313.042	-	-	-	-	-	-	-	-	0.04	0.05
Cadmium	226.502	-	-	-	-	0.03	-	-	0.02	-	-
Lead	220.353	0.17	-	-	-	-	-	-	-	-	-
Manganese	257.610	0.005	-	0.01	-	0.002	0.002	-	-	-	-
Selenium	196.026	0.23	-	-	-	0.09	-	-	-	-	-
Zinc	213.856	-	-	-	0.14	-	-	-	0.29	-	-

a - Dashes indicate that no interference was observed even when interferants were introduced at the following levels:

Al - 1000 mg/L,  
 Ca - 1000 mg/L,  
 Cr - 200 mg/L,  
 Cu - 200 mg/L,  
 Fe - 1000 mg/L,  
 Mg - 1000 mg/L,  
 Mn - 200 mg/L,  
 Tl - 200 mg/L,  
 V - 200 mg/L, and

b - The figures recorded as analyte concentrations are not the actual observed concentrations. To obtain those figures, add the listed concentration to the interferant figure.

Table 4. ICP Precision and Accuracy Data<sup>a</sup>

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
Cd	50	48	12	2.5	2.9	16	14	13	16
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se <sup>c</sup>	40	32	21.9	6	8.5	42	10	8.5	8.3

a - Not all elements were analyzed by all laboratories.

b - SD = standard deviation.

c - Results for Se are from two laboratories.

# ZINC IN SEDIMENTS (ICP)

## 1.0 Scope and Application

Inductively coupled plasma atomic emission spectroscopy (ICP) determines zinc and numerous other elements that are present in solution. In order to apply this technique to sediments, the samples must be digested with nitric acid and hydrogen peroxide prior to analysis.

Detection limits, sensitivity, and optimum concentration ranges for zinc, and other metals stable in a mixed standard solution with zinc, will vary with the sample aliquot size, the spectrophotometer being used, and possible matrix interferences. Based on the estimated detection limit of 2 µg/L for zinc in aqueous samples (Table 1), a sample size of 2 g, and a final digestate volume of 100 mL, the estimated detection limit for sediment samples is 100 µg/kg.

The method of standard addition (MSA) shall be used for the analysis of all sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required (see section 9).

This method should only be used by spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

This procedure is based on SW-846 Methods 3050 (for digestion) and 6010 for quantitation (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

A well-mixed, representative 1 to 2 g (wet weight) sample of sediment is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed using hydrochloric acid and diluted to volume.

**NOTE:** A separate sample shall be dried for a total solids determination in order to express the results on a dry-weight basis.

This instrumental method measures light emitted by zinc in the final sediment digest by optical spectrometry. The digested samples are nebulized and the resulting aerosol is transported to a plasma torch. Zinc-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes.

Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

The possibility of additional interferences named in section 3.0 should also be recognized and appropriate corrections made when necessary. The procedures that can be used for this purpose are described in section 9.

### 3.0 Interferences

Sediments represent diverse matrix types and samples from each location may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether the digestion procedure is appropriate for a specific sediment sample or there are matrix or other effects interfering with the analysis of the resultant sediment digestate.

#### 3.1 Spectral Interferences

Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multi-element instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferants can be assumed.

The magnitude of the interference effects summarized in Table 2 are expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that Zn is to be determined (at 213.856 nm) in a sample containing approximately 10 mg/L of Cu. According to Table 2, 100 mg/L of Cu would yield a false signal for Zn equivalent to approximately 0.14 mg/L. Therefore, the presence of 10 mg/L of Cu would result in a false signal for Zn equivalent to approximately 0.014 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, and argon flow rate.

The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

### 3.2 Physical Interferences

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Further, it has been reported that better control of the argon flow rate improves instrument performance. Improved argon flow rate control can be accomplished with the use of mass flow controllers.

### 3.3 Chemical Interferences

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, etc.), buffering of the sample, matrix matching, and standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Drying oven, capable of maintaining 30° C.
4. Thermometer, 0 to 200° C.
5. Centrifuge and centrifuge tubes.
6. Inductively coupled argon plasma emission spectrometer.
7. Computer-controlled emission spectrometer with background correction.
8. Radio frequency generator.
9. Argon gas supply, welding grade or better.

### 4.2 Materials

1. Conical Phillips beakers, 250 mL, or equivalent.
2. Watch glasses.
3. Whatman No. 41 filter paper, or equivalent.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.

3. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
4. Hydrogen peroxide, 30% (H<sub>2</sub>O<sub>2</sub>). Oxidant should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the H<sub>2</sub>O<sub>2</sub> is <MDL, then the acid can be used.
5. Nitric acid (1:1). Add 500 mL concentrated HNO<sub>3</sub> to 400 mL Type II water. Dilute to 1 liter with Type II water.
6. Hydrochloric acid (1:1). Add 500 mL concentrated HCl to 400 mL Type II water. Dilute to 1 liter with Type II water.
7. Standard stock solutions. May be purchased or prepared from ultrahigh purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hr at 105° C, unless otherwise specified.

**CAUTION:** Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

8. Beryllium standard stock solution (100 µg/mL). Dissolve 1.970 g BeSO<sub>4</sub>·4H<sub>2</sub>O (analytical reagent grade, undried), in 100 mL of Type II water, add 10.0 ml concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
9. Cadmium standard stock solution (100 µg/mL). Dissolve 0.1100 g CdO (analytical reagent grade) in a minimum amount of 1:1 HNO<sub>3</sub>. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
10. Lead standard stock solution (100 µg/mL). Dissolve 0.1600 g Pb(NO<sub>3</sub>)<sub>2</sub> (analytical reagent grade) in a minimum amount of 1:1 HNO<sub>3</sub>. Add 10 mL 1:1 HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
11. Manganese standard stock solution (100 µg/mL). Dissolve 0.1000 g of manganese metal, in an acid mixture of 10 mL concentrated HCl and 1 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
12. Selenium standard stock solution (100 µg/mL). Dissolve 0.1700 g H<sub>2</sub>SeO<sub>3</sub> (analytical reagent grade, undried) in 100 mL of Type II water. Dilute to 1 liter with Type II water.
13. Zinc standard stock solution (100 µg/mL). Dissolve 0.1200 g ZnO in a minimum amount of 1:1 HNO<sub>3</sub>. Add 10.0 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
14. Mixed calibration standard solutions. Care should be taken when preparing mixed standards for ICP analysis to ensure that the elements

in the final mixed standard are compatible and stable together. One set of mixed calibration standards that has been found to be useful is listed in Table 3. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities.

To prepare the mixed calibration standard for zinc, combine appropriate volumes of the individual stock solutions indicated in Table 3 in volumetric flask. Add 2 mL 1:1 HNO<sub>3</sub> and 10 mL of 1:1 HCl and dilute to 100 mL with Type II water. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see section 9.9) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Si
IV	Al, Ca, Cr, K, Na, and Ni

**NOTE:** Premixed standard solutions (traceable to NIST) containing the combined elements as listed in solutions I through IV are available from a number of commercial vendors.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Since field-moist samples are used in the determination, preservation of the sample is not practical. Therefore, analysis should begin as soon as possible after sample collection. A holding time of 6 months is generally cited for this parameter. Samples may be stored for a longer period of time by air-drying or freezing. However, these samples should not be used for the preparation of sediment elutriates because the process of freezing and thawing the samples may influence the migration potential of sediment-associated constituents.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of samples to be analyzed for zinc in sediments.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^\circ \text{C}$ .

The oven or hot plate should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^\circ \text{C}$ .

Prepare a calibration blank (see section 9.5.1) and at least three mixed calibration standards in the appropriate concentration range to correlate zinc concentrations with the ICP's linear response range. Prepare standards for instrument calibration as instructed in section 5.14. Match the sample matrix and that of the standards as closely as possible.

Calibrate the instrument according to the instrument manufacturer's recommended procedures using typical mixed calibration standard solutions. Flush the system with the calibration blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

## 8.0 Procedure

### 8.1 Sample Digestion

1. Weigh a 1.00 to 2.00 g aliquot of the homogenized, field-moist sediment to the nearest 0.01 g and quantitatively transfer the sample to a 250 mL conical beaker.
2. Add 10 mL of 1:1 HNO<sub>3</sub>, mix the slurry, and cover with a watch glass.
3. Heat the sample to 95° C and reflux for 10 to 15 min without boiling.
4. Allow the sample to cool. Add 5 mL of concentrated HNO<sub>3</sub>, replace the watch glass, and reflux for 30 min. Repeat this last step to ensure complete oxidation of the sample. Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.
5. After the sample has cooled, add 2 mL of Type II water and 3 mL of 30% H<sub>2</sub>O<sub>2</sub>. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Heat until effervescence subsides. Allow the beaker to cool.

**NOTE:** Exercise care to ensure that sample is not lost due to excessively vigorous effervescence.

6. Continue to add 30% H<sub>2</sub>O<sub>2</sub> in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

**NOTE:** The total volume of the 30% H<sub>2</sub>O<sub>2</sub> should not exceed 10 mL.

7. Add 5 mL of concentrated HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and reflux for an additional 15 min without boiling. After cooling, dilute to 100 mL with Type II water.
8. Suspended particulates should be removed by filtration, by centrifugation, or by allowing the sample to settle prior to analysis.
  - a. Filtration: Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.
  - b. Centrifugation: Centrifugation at 2,000 to 3,000 rpm for 10 min is usually sufficient to clear the supernatant.

9. The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO<sub>3</sub>. The sample is now ready for analysis.

## 8.2 Sample Analysis

1. The analyst should follow the instructions provided by the instrument's manufacturer. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range where coordination factors are valid. The analyst must: (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.
2. Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this conditions.
3. Flush the system with the calibration blank solution for at least 1 min before the analysis of each sample. Analyze samples.

**NOTE:** Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for zinc in sediments is 30 mg/kg (dry weight).

The detection limit specified in this method is presented to account for typical sediment background contents of chromium in the Great Lakes.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured arsenic concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards 2704 - Buffalo River sediment and 1646 - Estuarine sediment, should be run to monitor the performance of the ICP and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a routine sediment sample collected and homogenized in bulk that has undergone multiple analyses by the analytical laboratory. Alternately, a LCS can be created by spiking a known quantity of the contaminant(s) of concern into a clean sediment, homogenizing the bulk sample, followed by multiple analyses at the analytical laboratory. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

## 9.5 Blanks

Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

### 9.5.1 Calibration Blank

The calibration blank is prepared by diluting 2 mL of 1:1 HNO<sub>3</sub> and of 1:1 HCl to 100 mL with Type II water. Prepare a sufficient quantity to flush the system between standards and samples.

The calibration blank should be analyzed prior to routine sample analysis, after every 10 samples, and at the end of the analytical run. The measured concentration in the calibration blank should be less than or equal to the method detection limit.

### 9.5.2 Reagent Blank

The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.7 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - zinc, to a 1-2 g sample aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have a relative percent difference (RPD) of  $\leq 20\%$ .

## 9.8 Interference Check Sample

The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the method detection limit for each element. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

The interference check sample should be analyzed at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Results should be within  $\pm 20\%$  of the known concentration.

## 9.9 Calibration Control Sample

A calibration control sample should be prepared in the same acid matrix as the calibration standards at 10 times the method detection limit. This sample should be prepared in accordance with the instructions provided by the supplier. The calibration control sample is used to verify the integrity of the calibration standards on a weekly basis.

## 9.10 Recommended Tests

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests will ensure the analyst that neither positive nor

negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

### 9.10.1 Serial Dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution should agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

### 9.10.2 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 10.0 Method Performance

In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was  $9 \pm 2\%$ . The mean percent recovery of spiked elements for all wastes was  $93 \pm 6\%$ . Spike levels ranged from 100  $\mu\text{g/L}$  to 100  $\text{mg/L}$ . The wastes included sludges and industrial wastewaters.

## 11.0 Calculations and Reporting

If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in  $\mu\text{g/kg}$  with up to three significant figures.

The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Winge, R.K., V.J. Peterson, and V.A. Fassel. 1979. Inductively coupled plasma-atomic emission spectroscopy: Prominent lines, final report, March 1977 - February 1978, Ames laboratory, Ames, IA. EPA-600/4-79-017. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Table 1. Recommended Wavelengths and Estimated Instrumental Detection Limits.

Element	Wavelength <sup>a</sup> (nm)	Estimated Detection Limit <sup>b</sup> (µg/L)
Beryllium	313.042	0.3
Cadmium	226.502	4
Lead	220.353	42
Manganese	257.610	2
Selenium	196.026	75
Zinc	213.856	2

a - The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see section 3.1).

b - The estimated instrumental detection limits are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

Table 2. Analyte Concentration Equivalents arising from Interference at the 100 mg/L Level.

Analyte	Wavelength (nm)	Interferant <sup>a,b</sup>									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Mi	Tl	V
Beryllium	313.042	-	-	-	-	-	-	-	-	0.04	0.05
Cadmium	226.502	-	-	-	-	0.03	-	-	0.02	-	-
Lead	220.353	0.17	-	-	-	-	-	-	-	-	-
Manganese	257.610	0.005	-	0.01	-	0.002	0.002	-	-	-	-
Selenium	196.026	0.23	-	-	-	0.09	-	-	-	-	-
Zinc	213.856	-	-	-	0.14	-	-	-	0.29	-	-

a - Dashes indicate that no interference was observed even when interferants were introduced at the following levels:

Al - 1000 mg/L,  
 Ca - 1000 mg/L,  
 Cr - 200 mg/L,  
 Cu - 200 mg/L,  
 Fe - 1000 mg/L,  
 Mg - 1000 mg/L,  
 Mn - 200 mg/L,  
 Tl - 200 mg/L,  
 V - 200 mg/L, and

b - The figures recorded as analyte concentrations are not the actual observed concentrations. To obtain those figures, add the listed concentration to the interferant figure.

Table 4. ICP Precision and Accuracy Data<sup>a</sup>

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
Cd	50	48	12	2.5	2.9	16	14	13	16
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se <sup>c</sup>	40	32	21.9	6	8.5	42	10	8.5	8.3

a - Not all elements were analyzed by all laboratories.

b - SD = standard deviation.

c - Results for Se are from two laboratories.

# TOTAL ORGANIC CARBON IN SEDIMENTS

## 1.0 Scope and Application

This method is applicable to the determination of total organic carbon (TOC) content in sediment samples. TOC is often used as a surrogate indicator for the presence of organic pollutants.

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

Inorganic carbonates are removed from a well mixed aliquot of sediment by acidification with phosphoric acid. After carbonate removal, the sample is dried and ground to pass through a 80-mesh sieve or finer. An aliquot is then oxidized at temperatures greater than 1,000° C with catalysts as specified by the instrument manufacturer. The evolved CO<sub>2</sub> is determined by thermal conductivity (TC) or infrared (IR) spectroscopy.

## 3.0 Interferences

Non-representative particulates such as leaves, sticks, fish and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.

Carbonate and bicarbonate carbon represent an interference and must therefore, be removed prior to sample analysis. Incomplete removal of carbonate or bicarbonates will lead to total organic carbon contents that are biased high.

Removal of inorganic carbonates by acidification may lead to the loss of volatile organic compounds/substances from the sample. Additionally, drying the sample may lead to the loss of volatile organic compounds/substances.

Ambient CO<sub>2</sub> not associated with the sample present possible gaseous interferences. Care must be taken with the blank to hold CO<sub>2</sub> below the method detection limit. The use of high purity carrier gas or helium helps reduce CO<sub>2</sub>.

Sediment residue can accumulate at the top of the combustion column. The column should be cleaned if sufficient residue accumulates to affect analytical results.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

**NOTE:** This list is generic for total carbon analysis. The specific requirements will vary with the instrument. Some additional apparatus may be required; other equipment may not be needed.

1. Analytical balance, capable of weighing to  $\pm 0.001$  mg ( $\pm 1$   $\mu$ g).
2. Analytical balance calibration weights, 3-5 weights covering expected weight range.
3. Brass sieve, 80-mesh or finer.
4. Carbon analyzer with infrared detector.
5. Convection oven.
6. Desiccator and desiccant.
7. Mortar and pestle, agate or porcelain.
8. Thermometer, 0 to 200° C range.

### 4.2 Materials

1. Absorbents (as needed).
2. Carrier gases with in-line filter (as needed).
3. Catalysts and combustion accelerators (as needed).
4. Combustion vehicles. Vials, crucibles, boats, or tin sample capsules.
5. Evaporating dishes, porcelain, 90 mm, 100 mL capacity. (aluminum, Vycor, or platinum weighing dishes may be substituted and smaller size dishes may be used, if required.)
6. Oxygen with in-line filter (high purity; >99.5% @ 30 psi).

## 5.0 Reagents and Standards

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated phosphoric acid, reagent grade ( $H_3PO_4$ ).

3. Phosphoric acid, 10%. Add 100 mL concentrated  $\text{H}_3\text{PO}_4$  to 700 mL Type II water. Dilute to 1 liter with Type II water.

## 6.0 Sample Handling and Preservation

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Since field-moist samples are used in the determination, preservation of the sample is not practical. Therefore, analysis should begin as soon as possible after sample collection. A holding time of 28 days is generally cited for this parameter.

Samples should be stored under refrigerated conditions ( $4^\circ\text{C}$ ) to minimize decomposition of organics between sample collection and sample analysis.

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of samples to be analyzed for total organic carbon in sediments.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically to ensure that they are measuring temperature accurately.

The oven should be monitored to ensure that temperature fluctuation does not exceed  $\pm 5^\circ\text{C}$ .

Follow the instrument manufacturer's instructions regarding calibration and standardization. In general, the instrument should be calibrated at least once per day or once per batch of samples, whichever is more frequent. Use either NIST reference materials or standards supplied by the manufacturer and approved by the laboratory or QA manager. The concentration range of the standards must be representative of the C concentrations in the sediment samples.

In general, the calibration procedure for carbon analyzers is as follows:

- a. Analyze 3 blank samples to determine instrument stability.
- b. If a stable baseline is obtained, run 3 to 5 conditioning analyses.

**NOTE:** Acetonitrile ( $C_2H_3N$ ) is commonly used as the conditioner sample.

- c. Analyze 3 to 5 samples of a known standard.
- d. Analyze a blank sample to check for analyte memory effects.

## 8.0 Procedure

### 8.1 Sample Preparation

1. Weigh a 5 g aliquot of the homogenized, field-moist sediment to the nearest gram and transfer the sample to a 100 mL evaporating dish.
2. Dry the sample overnight at 60° C.
3. Break up dried sediment pellet with a spatula and add several drops of 10% phosphoric acid.
4. Continue adding 10% phosphoric acid until all effervescence is completed.

**NOTE:** Do not add too much 10% phosphoric acid in any given increment since this may cause loss of sample due to frothing.

5. Add 2 mL of 10% phosphoric acid, stir the sample, and allow to sit covered for 4 hours.

**NOTE:** The sample should be stirred every hour.

6. Dry the sample overnight at 60° C.
7. Using a mortar and pestle, grind sample such that the whole sample passes through a 80-mesh sieve or finer.
8. Store ground sample in desiccator until ready for analysis.

## 8.2 Sample Analysis

1. Weigh approximately 100 mg of dried homogenized sediment into an appropriate tared combustion vehicle. Record weight of sample.

**NOTE:** If high organic carbon contents are suspected for a given sample, sample size may have to be reduced to approximately 20 mg of dried sediment.

2. Perform analysis as recommended by instrument manufacturer.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for total organic carbon in sediments is 0.1%.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured total organic carbon concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards 2704 - Buffalo River sediment and 1646 - Estuarine sediment, should be run to monitor the performance of the carbon analyzer and to assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

## 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a routine sediment sample collected and homogenized in bulk that has undergone multiple analyses by the analytical laboratory. Alternately, a LCS can be created by spiking a known quantity of the contaminant(s) of concern into a clean sediment, homogenizing the bulk sample, followed by multiple analyses at the analytical laboratory. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

## 9.5 Blanks

A minimum of one reagent blank (an empty combustion vessel containing any combustion catalysts/accelerators used during routine sample analysis) per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 10.0 Method Performance

In a study involving a quality control check sample for soils, for 41 observations, the mean, standard deviation, and coefficient of variation for total carbon content was 11.38, 0.062, and 5.5%, respectively (USDA-SCS, 1992).

## 11.0 Calculations and Reporting

Calculations should be performed following instrument manufacturer's instructions.

Total organic carbon should be reported on a weight percent basis.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. Department of Agriculture - Soil Conservation Service. 1992. Soil Survey Laboratory Methods Manual. Soil Survey Investigations Report No. 42. Version 2.0. National Soil Survey Laboratory, Lincoln, NE.

# TOTAL PETROLEUM HYDROCARBONS IN SEDIMENTS (SPECTROPHOTOMETRIC, INFRARED)

## 1.0 Scope and Application

This method is appropriate for the determination of fluorocarbon-113 extractable petroleum hydrocarbons from sediment samples. It should be noted that this method will change upon identification and approval of an environmentally friendly solvent.

This method can be used when relatively polar, heavy petroleum fractions are present, or when the levels of non-volatile greases challenge the solubility limit of the solvent.

The method is not recommended for measurement of low-boiling fractions that volatilize at temperatures below 70° C.

This method is based on a combination of EPA SW-846 Method 9071 (USEPA, 1986) and EPA Method 418.1 (USEPA, 1983).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

A 20 g sample of wet sediment, with a known dry-solids content, is acidified to pH 2 with hydrochloric acid. Magnesium sulfate monohydrate, which will combine with 75% of its own weight in water, is then added to dry the sample.

After drying, petroleum hydrocarbons are extracted from the sample using Fluorocarbon 113. Infrared analysis of the extract at 2930  $\text{cm}^{-1}$  is performed and total petroleum hydrocarbon contents are determined by direct comparison with standards.

## 3.0 Interferences

Total petroleum hydrocarbons (TPHs) are operationally defined by the extraction procedure and the analytical technique.

The method is not considered applicable to light hydrocarbons that volatilize below 70° C. Also, some crude oils and heavy fuel oils that are not soluble in fluorocarbon-113 will have low recoveries.

The rate and time of extraction in the Soxhlet apparatus should be strictly controlled because of varying solubilities of different greases.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Infrared spectrophotometer, scanning or fixed wavelength, for measurement around 2930  $\text{cm}^{-1}$ .
4. Magnetic stirrer, with Teflon coated stirring bars.
5. Mortar and pestle.
6. Soxhlet extraction apparatus.
7. Vacuum pump or other source of vacuum.

### 4.2 Materials

1. Separatory funnel with Teflon stopcock, 2000 mL.
2. Beakers, glass, 150 mL.
3. Cells, 10 mm, 50 mm, and 100 mm pathlength, sodium chloride or infrared grade glass.
4. Extraction thimbles, paper.
5. Glass bottles with stoppers, 50 mL.
6. Glass wool or beads.
7. Volumetric flasks, class A, 200 mL.
8. Volumetric flasks, class A, 100 mL.
9. Whatman filter paper No. 40, 11 cm.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.

2. Fluorocarbon-113 (1,1,2-trichloro-1,2,2-trifluoroethane), boiling point 47° C.

**NOTE:** The solvent should leave no measurable residue on evaporation. Redistill if necessary.

3. Concentrated hydrochloric acid (HCl), reagent grade. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
4. Hydrochloric acid (HCl), 1:1. Mix equal volumes of concentrated HCl and Type II water.
5. Magnesium sulfate monohydrate ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ). Prepare  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  by spreading a thin layer in a dish and drying in an oven at 150° C overnight.
6. Silica gel, 60-200 mesh, Davidson Grade 950, or equivalent. Should contain 1-2% water as defined by residue test at 130° C. Adjust by overnight equilibration, if needed.
7. Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), anhydrous crystal.
8. Reference oil used for calibration mixtures. Pipet 15.0 mL n-hexadecane ( $\text{C}_{16}\text{H}_{34}$ ), 15.0 mL isooctane ( $\text{C}_8\text{H}_{18}$ ), and 10.0 mL chlorobenzene ( $\text{C}_6\text{H}_5\text{Cl}$ ) into a 50 mL glass-stoppered bottle. Maintain the integrity of the mixture by keeping stoppered except when withdrawing aliquots.
9. Reference oil stock solution. Pipet 1.0 mL reference oil into a tared 200 mL volumetric flask and immediately stopper. Weigh and dilute to volume with fluorocarbon-113.
10. Reference oil working standards. Pipet appropriate volumes of stock standard into 100 mL volumetric flasks according to the cell pathlength to be used. Dilute to volume with fluorocarbon-113. Calculate concentration of standards from the stock standard.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

It is recommended that only field-moist samples be used in the TPH analysis.

A holding time of 28 days after sample collection is generally cited for this parameter.

The sample should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Sample aliquots to be analyzed for TPH should be collected and stored in glass bottles.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Select appropriate working standards and cell pathlength based on the expected total petroleum hydrocarbon concentration in the final sediment extract. The following information is presented as a guide for selecting a suitable cell pathlength:

<u>Pathlength</u>	<u>Range</u>
10 mm	2-40 mg
50 mm	0.5-8 mg
100 mm	0.1-4 mg

Calibrate the instrument for the appropriate cells using a series of working standards. It is not necessary to add silica gel to the standards.

Scan the standards from 3200 to 2700  $\text{cm}^{-1}$  using a scanning infrared spectrophotometer. Fluorocarbon-113 should be used in the reference beam of a dual beam instrument or to zero a single beam instrument. The absorbance of the 2930  $\text{cm}^{-1}$  peak should be used to construct a standard curve.

## 8.0 Procedure

1. Weigh out  $20 \pm 0.5$  g of the homogenized, field-moist sediment and place in a 150 mL beaker.

**NOTE:** The dry-solids content of the sediment should be determined on a separate sample aliquot.

2. Acidify the sample to pH 2 with approximately 0.3 mL concentrated HCl.
3. Add 25 g prepared  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  to the acidified sample and stir to create a smooth paste.
4. Spread the paste on the sides of the beaker to facilitate drying. Let the paste stand 15-30 minutes or until the material has solidified.
5. Transfer the solids to a mortar and grind to a fine powder.
6. Add the powder to a paper extraction thimble.
7. Wipe both the beaker and the mortar with pieces of filter paper moistened with solvent and add the paper to the thimble.
8. Fill the thimble with glass wool (or glass beads).
9. Place the thimble in a Soxhlet apparatus and extract using fluorocarbon-113 at a rate of 20 cycles/hour for 4 hours.
10. Using grease-free cotton, filter the extract into a volumetric flask. Dilute to volume with fluorocarbon-113.

**NOTE:** If the final filtrate is turbid, refilter into a clean flask.

**NOTE:** If an emulsion forms, it can be broken by filtering the extract through 1 g sodium sulfate in a filter paper cone. Additional 1 g portions of sodium sulfate can be used as required.

11. Discard about 5-10 mL solution from the volumetric flask. Add 3 g silica gel and a stirring bar.
12. Stopper the volumetric flask and stir the solution for a minimum of 5 min on a magnetic stirrer.
13. After the silica gel has settled in the sample extract, fill a clean cell with solution and determine the absorbance of the extract.

**NOTE:** If the absorbance exceeds 0.8, prepare an appropriate dilution and reanalyze the sample.

**NOTE:** The possibility that the absorptive capacity of the silica gel has been exceeded can be tested at this point by adding another 3.0 g silica gel to the extract and repeating the treatment and determination.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for TPH in sediments is 5000 µg/kg.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured TPH concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a routine sediment sample collected and homogenized in bulk that has undergone multiple analyses by the analytical laboratory. Alternately, a LCS can be created by spiking a known quantity of the contaminant(s) of concern into a clean sediment, homogenizing the bulk sample, followed by multiple analyses at the analytical laboratory. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

## 9.5 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the instrument detection limit.

## 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.7 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte (i.e., reference oil), in this case - TPH, to the 20 g aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 20\%$ .

## 10.0 Method Performance

The analysis of six replicate sludge samples extracted with this method and analyzed in a single laboratory produced a standard deviation of 4.6%.

## 11.0 Calculations and Reporting

Determine the concentration of petroleum hydrocarbons in the extract by comparing the response against the calibration plot. The concentration of total petroleum hydrocarbons in the original sediment sample can then be calculated as follows:

$$\text{TPH, mg/kg (wet weight)} = \frac{X \times Y \times 1000}{g}$$

where:

X = the concentration of total petroleum hydrocarbons in the final sediment extract, mg/L.

Y = volume of final sediment extract, L.

g = wet weight of sediment extracted, g.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

Blum, K.A. and M.J. Taras. 1968. Determination of Emulsifying Oil in Industrial Wastewater" JWPCF Research Supplement 40:R404.

U.S. Environmental Protection Agency. 1983. Methods for the Chemical Analysis of Water and Wastes. EPA-600/4-79-020. U.S. Environmental Protection Agency Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

U.S. Environmental Protection Agency. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

# PHENOLICS IN SEDIMENTS (COLORIMETRIC, AUTOMATED 4-AAP)

## 1.0 Scope and Application

This method is applicable to the determination of phenolic compounds in sediment samples. The minimum detectable concentration of phenol in the final sediment distillate is 2 µg/L and the working range of the method is 2 to 500 µg/L when using phenol as a standard. The useful range of the procedure can be extended by modifying the sample size or diluting the final sediment distillate prior to analysis.

This method is based on SW-846 Method 9066 (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

Phenolic compounds are separated from the sediment sample matrix by distillation under acidic conditions (pH <4.0). The phenolic compounds in the distillate are then reacted with alkaline ferricyanide ( $K_3Fe(CN)_6$ ) and 4-aminoantipyrine (4-AAP) to form a red complex which is measured at 505 or 520 nm.

## 3.0 Interferences

Color and turbidity in the original sample can interfere with this colorimetric procedure. Color interference is eliminated by distilling the phenolic compounds from the original sample prior to analysis. Turbidity is removed by sample filtration prior to analysis.

Oxidizing agents, such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate (see section 5.0, item 3). If chlorine is not removed, the phenolic compounds may be partially oxidized and the sample results may be biased low.

Background contamination from plastic tubing and sample containers is eliminated by filling the wash receptacle by siphon (using Kel-F tubing) and using glass tubes for the samples and standards.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Distillation apparatus, all glass, consisting of a 1 liter pyrex distillation flask and a Graham condenser.
4. pH meter.
5. Automated continuous-flow analytical instrument with:
  - a. sampler equipped with continuous mixer,
  - b. manifold,
  - c. proportioning pump II or III,
  - d. heating bath with distillation coil,
  - e. distillation head,
  - f. colorimeter equipped with a 50 mm flowcell and 505 or 520 nm filter, and
  - g. recorder.

### 4.2 Materials

1. Volumetric flasks, class A, 1 L.
2. Volumetric flasks, class A, 100 mL.
3. Whatman filter paper no. 12.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. 4-Aminoantipyrine (4-AAP). Dissolve 0.65 g of 4-aminoantipyrine in 800 mL of Type II water. Dilute to 1 liter with Type II water. Prepare fresh daily.
3. Ferrous ammonium sulfate ( $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ). Dissolve 1.1 g ferrous ammonium sulfate in 500 mL of Type II water containing 1 mL

concentrated  $\text{H}_2\text{SO}_4$ . Dilute to 1 liter with freshly boiled and cooled Type II water.

4. Buffered potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ). Dissolve 2.0 g potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ), 3.1 g boric acid ( $\text{H}_3\text{BO}_3$ ), and 3.75 g potassium chloride (KCl) in 800 mL of Type II water. Adjust to pH of 10.3 with 1 N sodium hydroxide. Dilute to 1 liter with Type II water. Add 0.5 mL of Brij-35 (available from Technicon). Prepare fresh weekly.

**NOTE:** Brij-35 is a wetting agent and is a proprietary Technicon product.

5. Sodium hydroxide (NaOH), 1 N. Dissolve 40 g NaOH in 500 mL of Type II water. Cool. Dilute to 1 liter with Type II water.
6. Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ), reagent grade. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
7. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), 1 N. Add 28 mL concentrated  $\text{H}_2\text{SO}_4$  to 900 mL of Type II water. Dilute to 1 liter with Type II water.
8. Phenol stock solution. Dissolve 1.00 g phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) in 500 mL of Type II water. Dilute to 1 liter with Type II water. Add 0.5 mL concentrated  $\text{H}_2\text{SO}_4$  as preservative (1.0 mg/mL phenol).

**CAUTION:** This solution is toxic.

9. Phenol standard solution A. Dilute 10.0 mL of phenol stock solution to 1 liter with Type II water (0.01 mg/mL phenol).
10. Phenol standard solution B. Dilute 100.0 mL of phenol standard solution A to 1 liter with Type II water (0.001 mg/mL phenol).
11. Phenol standard solution C. Dilute 100.00 mL of phenol standard solution B to 1 liter with Type II water (0.0001 mg/mL phenol).

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

It is recommended that only field-moist samples be used in the phenol analysis. This recommendation is based on the fact that dried samples may lose phenol by biological degradation. Also, both air-dried and frozen samples may lose phenol during the drying and/or freezing cycles.

A holding time of 28 days after sample collection is generally cited for this parameter.

The sample should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Sample aliquots to be analyzed for phenolic compounds should be collected and stored in glass bottles.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Calibration curves must be composed of a minimum of a blank and three standards. A separate calibration curve should be prepared for every hour of continuous sample analysis.

Using standard solution A, B, or C, prepare the following standards in 100 mL volumetric flasks:

<u>Standard Solution (mL)</u>	<u>Concentration (µg/L)</u>
<u>Solution C</u>	
1.0	1.0
2.0	2.0
3.0	3.0
5.0	5.0
<u>Solution B</u>	
1.0	10.0
2.0	20.0
5.0	50.0
10.0	100.0
<u>Solution A</u>	
2.0	200.0
3.0	300.0
5.0	500.0

Each standard should be preserved by adding 2 drops of concentrated  $\text{H}_2\text{SO}_4$  to 100.0 mL.

Prepare a linear standard curve by plotting peak heights of standards against concentration values.

## 8.0 Procedure

1. Place 550 mL of Type II water into a 1-L pyrex distillation flask.
2. Quantitatively transfer a 10 to 50 g aliquot of the sample to be analyzed to the distillation flask.

**NOTE:** The amount of sediment used should not contain more than 50  $\mu\text{g}$  phenolic compounds.

3. Adjust the pH of the sample to approximately 4 with the addition of 1 N sulfuric acid.
4. Add a few boiling stones.
5. Attach the condenser and distill over 500 mL of distillate.

**NOTE:** If the sample distillate is turbid, it should be filtered through a prewashed membrane filter prior to analysis.

**NOTE:** If oil is present in the final distillate, filter the sample through two thicknesses of dry No. 12 Whatman filter paper to remove the oil.

6. Set up a AutoAnalyzer manifold with the following flow rates:

Air	0.32 mL/min.
Sample	2.00 mL/min.
Distilling solution	0.42 mL/min.
Waste from still	0.42 mL/min.
Air	0.32 mL/min.
Resample waste	1.00 mL/min.
Resample	1.2 mL/min.
4-AAP	0.23 mL/min.
Buffered potassium ferricyanide	0.23 mL/min.
Waste from F/C	1.0 mL/min.

7. Fill the wash receptacle by siphon. Use Kel-F tubing with a fast flow (1 liter/hr).
8. Allow colorimeter and recorder to warm up for 30 min.
9. Run a baseline with all reagents feeding Type II water through the sample line.

**NOTE:** Use polyethylene tubing for sample line.

**NOTE:** When new tubing is used, about 2 hours may be required to flush residual phenol from the tubing and obtain a stable baseline.

10. Place appropriate standards in the sampler in order of decreasing concentration.
11. Complete loading of the sampler tray with unknown and quality assurance/quality control samples in glass tubes.
12. Run with sensitivity setting at full scale or 500.
13. When the baseline becomes steady, switch sample from Type II water to samples and begin analysis.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for phenolics in sediments is 1000 µg/kg.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured phenolic concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per

analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

#### 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a routine sediment sample collected and homogenized in bulk that has undergone multiple analyses by the analytical laboratory. Alternately, a LCS can be created by spiking a known quantity of the contaminant(s) of concern into a clean sediment, homogenizing the bulk sample, followed by multiple analyses at the analytical laboratory. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

#### 9.5 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the instrument detection limit.

#### 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

#### 9.7 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - phenolics, to the 10 to 50 g aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision

between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 20\%$ .

## 10.0 Method Performance

Precision and accuracy information are not available at this time.

## 11.0 Calculations and Reporting

The concentration of phenolic compounds in the original sediment sample can be calculated as follows:

$$\text{Phenol, } \mu\text{g/kg (wet weight)} = \frac{A \times B \times 1000}{g}$$

where:

A = phenol concentration in distillate,  $\mu\text{g/L}$

B = total volume of final distillate, L (0.5 L as written)

g = wet weight of sediment sample, g.

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. Method 510. 14th Edition, APHA, New York, New York. p. 574.

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

Gales, M.E., and R. L. Booth. 1976. Automated 4-AAP Phenolic Method. AWWA 68:540.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

# TOTAL POLYCHLORINATED BIPHENYLS (PCBs) AND PESTICIDES IN SEDIMENTS

## 1.0 Scope and Application

This method is suitable for the determination of chlorinated pesticides and PCB congeners in sediment samples. Table 1 presents the PCB congeners most commonly found in the environment while Table 2 list the pesticides of concern in the Great Lakes. All these compounds may be determined using this method.

This procedure is based on a National Oceanic and Atmospheric Administration (NOAA) method for the determination of Extractable Toxic Organic Compounds in marine sediments (NOAA, 1985).

The extracts produced from this method (sections 8.1 through 8.6) can be used in the determination of PCBs, pesticides, and polynuclear aromatic hydrocarbons (PAHs).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

The sample is extracted with methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) and sodium sulfate ( $\text{Na}_2\text{SO}_4$ ). The resultant extract is cleaned-up with silica gel and alumina. Additional clean-up steps to remove biological macromolecules are performed using Sephadex LH-20. PCB congeners and pesticides are then quantified using a glass capillary column to resolve all congeners and gas chromatography/electron capture detector (GC/ECD). The concentrations of 20 congeners (Table 3) will be summed to determine the total PCB content in the sediment.

The same extract used to analyze for PCBs and pesticides can be used to analyze polynuclear aromatic hydrocarbons (PAHs) using gas chromatography/mass spectrometry (GC/MS). The method for PAH determination is provided in this methods manual.

Table 1. PCB Congeners Commonly Identified in the Great Lakes.

BZ#	Structure	BZ#	Structure
1	2-chlorobiphenyl	105	2,3,3',4,4'-pentachlorobiphenyl
3	4-chlorobiphenyl	107	2,3,3',4',5-pentachlorobiphenyl
4	2,2'-dichlorobiphenyl	115	2,3,4,4',6-pentachlorobiphenyl
5	2,3-dichlorobiphenyl	119	2,3',4,4',6-pentachlorobiphenyl
6	2,3'-dichlorobiphenyl	122	2',3,3',4,5-pentachlorobiphenyl
9	2,5-dichlorobiphenyl	123	2',3,4,4',5-pentachlorobiphenyl
12	3,4-dichlorobiphenyl	128	2,2',3,3',4,4'-hexachlorobiphenyl
15	4,4'-dichlorobiphenyl	129	2,2',3,3',4,5-hexachlorobiphenyl
16	2,2',3-trichlorobiphenyl	136	2,2',3,3',6,6'-hexachlorobiphenyl
18	2,2',5-trichlorobiphenyl	137	2,2',3,4,4',5-hexachlorobiphenyl
19	2,2',6-trichlorobiphenyl	138	2,2',3,4,4',5'-hexachlorobiphenyl
22	2,3,4'-trichlorobiphenyl	141	2,2',3,4,5,5'-hexachlorobiphenyl
25	2,3',4-trichlorobiphenyl	149	2,2',3,4',5',6-hexachlorobiphenyl
26	2,3',5-trichlorobiphenyl	151	2,2',3,5,5',6-hexachlorobiphenyl
27	2,3',6-trichlorobiphenyl	153	2,2',4,4',5,5'-hexachlorobiphenyl
28	2,4,4'-trichlorobiphenyl	157	2,3,3',4,4',5'-hexachlorobiphenyl
29	2,4,5-trichlorobiphenyl	158	2,3,3',4,4',6-hexachlorobiphenyl
31	2,4',5-trichlorobiphenyl	167	2,3',4,4',5,5'-hexachlorobiphenyl
37	3,4,4'-trichlorobiphenyl	170	2,2',3,3',4,4',5-heptachlorobiphenyl
40	2,2',3,3'-tetrachlorobiphenyl	171	2,2',3,3',4,4',6-heptachlorobiphenyl
41	2,2',3,4-tetrachlorobiphenyl	177	2,2',3,3',4,5,6-heptachlorobiphenyl
44	2,2',3,5'-tetrachlorobiphenyl	180	2,2',3,4,4',5,5'-heptachlorobiphenyl
47	2,2',4,4'-tetrachlorobiphenyl	183	2,2',3,4,4',5,6-heptachlorobiphenyl
49	2,2',4,5'-tetrachlorobiphenyl	185	2,2',3,4,5,5,6'-heptachlorobiphenyl
52	2,2',5,5'-tetrachlorobiphenyl	187	2,2',3,4',5,5',6-heptachlorobiphenyl
53	2,2',5,6'-tetrachlorobiphenyl	189	2,3,3',4,4',5,5'-heptachlorobiphenyl
56	2,3,3',4'-tetrachlorobiphenyl	190	2,3,3',4,4',5,6-heptachlorobiphenyl
66	2,3,4,4'-tetrachlorobiphenyl	191	2,3,3',4,4',5',6-heptachlorobiphenyl
70	2,3',4',5-tetrachlorobiphenyl	193	2,3,3',4',5,5',6-heptachlorobiphenyl
75	2,4,4',6-tetrachlorobiphenyl	194	2,2',3,3',4,4',5,5'-octachlorobiphenyl
77	3,3',4,4'-tetrachlorobiphenyl	195	2,2',3,3',4,4',5,6-octachlorobiphenyl
82	2,2',3,3',4-pentachlorobiphenyl	196	2,2',3,3',4,4',5',6-octachlorobiphenyl
83	2,2',3,3',5-pentachlorobiphenyl	198	2,2',3,3',4,5,5',6-octachlorobiphenyl
84	2,2',3,3',6-pentachlorobiphenyl	199	2,2',3,3',4,5,6,6'-octachlorobiphenyl
85	2,2',3,4,4'-pentachlorobiphenyl	200	2,2',3,3',4,5',6,6'-octachlorobiphenyl
87	2,2',3,4,5'-pentachlorobiphenyl	201	2,2',3,3',4',5,5',6-octachlorobiphenyl
91	2,2',3,4',6-pentachlorobiphenyl	202	2,2',3,3',5,5',6,6'-octachlorobiphenyl
92	2,2',3,5,5'-pentachlorobiphenyl	205	2,3,3',4,4',5,5',6-octachlorobiphenyl
95	2,2',3,5',6-pentachlorobiphenyl	206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl
97	2,2',3',4,5-pentachlorobiphenyl	207	2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl
99	2,2',4,4',5-pentachlorobiphenyl	208	2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl
101	2,2',4,5,5'-pentachlorobiphenyl		

Table 2. Pesticides of Concern in the Great Lakes.

aldrin	<u>trans</u> -nonachlor
α-chlordane	<u>o,p'</u> -DDE
dieldrin	<u>p,p'</u> -DDE
heptachlor	<u>o,p'</u> -DDD
heptachlor epoxide	<u>p,p'</u> -DDD
hexachlorobenzene	<u>o,p'</u> -DDT
lindane (γ-BHC)	<u>p,p'</u> -DDT
mirex	

Table 3. Twenty PCB Congeners to be Summed to Determine Total PCB Content<sup>a</sup>.

BZ#	Structure	BZ#	Structure
8	2,4'-dichlorobiphenyl	126	3,3',4,4',5-pentachlorobiphenyl
18	2,2',5-trichlorobiphenyl	128	2,2',3,3',4,4'-hexachlorobiphenyl
28	2,4,4'-trichlorobiphenyl	138	2,2',3,4,4',5'-hexachlorobiphenyl
44	2,2',3,5'-tetrachlorobiphenyl	153	2,2',4,4',5,5'-hexachlorobiphenyl
52	2,2',5,5'-tetrachlorobiphenyl	169	3,3',4,4',5,5'-hexachlorobiphenyl
66	2,3,4,4'-tetrachlorobiphenyl	170	2,2',3,3',4,4',5-heptachlorobiphenyl
77	3,3',4,4'-tetrachlorobiphenyl	180	2,2',3,4,4',5,5'-heptachlorobiphenyl
101	2,2',4,5,5'-pentachlorobiphenyl	187	2,2',3,4',5,5',6-heptachlorobiphenyl
105	2,3,3',4,4'-pentachlorobiphenyl	206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl
118	2,3',4,4',5-pentachlorobiphenyl	209	2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl

a = The selected congeners are a combination of those presented in the *Inland Testing Manual* (USEPA/USACE, 1998) and NOAA method (NOAA, 1985).

### 3.0 Interferences

Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large late-eluting peaks. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

Elemental sulfur contained in some bottom sediment extracts is also a major interference. This method removes S by the addition of elemental copper.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.001 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Centrifuge, capable of holding 250 mL centrifuge tubes and maintaining speeds of 1500 rpm.
4. Desiccator and desiccant. Desiccants generally used include: anhydrous calcium sulfate, silica gel, or phosphorus pentoxide. Indicating desiccants are preferable since they show when the desiccant needs to be changed or regenerated.
5. Gas chromatograph (GC) including:
  - a. dual capillary column inlet system,
  - b. autosampler,
  - c. cartridge tape unit, and
  - d. electron capture detector (ECD), two are needed.
6. Modified Kontes tube heater (block contains: Al inserts fitted to the 0.7 mL line of the tube tip and an Al-foil shroud).
7. Molecular sieve traps (for gas cylinder)

**NOTE:** One suggested source for the molecular sieve traps is Hydro-Purge model ASC-I, Coast Engineering Laboratory, Gardena, California.

8. Oxygen traps.
9. UV light source.
10. Water bath, capable of maintaining a temperature of  $80 \pm 2^\circ \text{C}$ .

### 4.2 Materials

1. Beakers, 250 mL, or equivalent.
2. Centrifuge tubes, 250 mL, amber, with Teflon™ caps.
3. Chromatography column with reservoir 250 mL, 19 mm ID, 30

cm.

4. Erlenmeyer flask, 500 mL, with stopper.
5. Erlenmeyer flask, 1 L, with stopper.
6. Funnel, curved-stem (curve must be glassblown).
7. Funnel, 200 mm OD, long-stem.
8. Funnel, powder.
9. GC column, silicon-coated fused silica capillary, DB-5, 30 m x 0.25 mm I.D.
10. GC column, silicon-coated fused silica capillary, DB-17HT, 30 m x 0.25 mm I.D.
11. Graduated cylinder, 500 mL.
12. Graduated cylinder, 100 mL.
13. Graduated cylinder, 50 mL.
14. Kontes concentrator tube, 25 mL, with stopper.
15. Snyder column, 3-ball.
16. Syringe, 2000  $\mu$ L.
17. Syringe, 800  $\mu$ L.
18. Syringe, 400  $\mu$ L.
19. Syringe, 200  $\mu$ L.
20. Syringe, 100  $\mu$ L.
21. Syringe, 50  $\mu$ L.
22. Syringe, 10  $\mu$ L.
23. Teflon wash-bottle, 500 mL (to be filled with  $\text{CH}_2\text{Cl}_2$ ).
24. Transfer pipets (Pasteur style) with rubber bulbs.
26. GC vials, 2 mL.
27. GC vials, 100  $\mu$ L, conical.
28. Volumetric flask, class A, 10 mL.
29. Volumetric pipet, 50 mL.

## 5.0 Reagents

1. Alumina, 80-200 mesh. Alumina should be activated at 120° C for 2 hr and then cooled to room temperature in a desiccator just before weighing and use.
2. Azulene, reagent grade ( $\text{C}_{15}\text{H}_{18}$ ).
3. Copper, reagent grade, fine granular. Copper should be activated < 1 hr before use. To activate copper, cover with concentrated. HCl and stir with a glass rod. Allow to stand for 5 min followed by washing twice with  $\text{CH}_3\text{OH}$  and then 3 times with  $\text{CH}_2\text{Cl}_2$ . Leave copper covered with  $\text{CH}_2\text{Cl}_2$  to avoid contact with air.
4. Helium, grade 4.5 (purified,  $\geq 99.995$  %).

5. Hexane, high purity (C<sub>6</sub>H<sub>14</sub>). Each solvent lot should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the solvent has a concentration <MDL, then the solvent can be used.
6. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
7. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
8. Methanol, high purity (CH<sub>3</sub>OH). Each solvent lot should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the solvent has a concentration <MDL, then the solvent can be used.
9. Methylene chloride (dichloromethane), high purity (CH<sub>2</sub>Cl<sub>2</sub>). Each solvent lot should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the solvent has a concentration <MDL, then the solvent can be used.
10. Pentane, high purity (C<sub>5</sub>H<sub>12</sub>). Each solvent lot should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the solvent has a concentration <MDL, then the solvent can be used.
11. Perylene, reagent grade (C<sub>20</sub>H<sub>12</sub>).
12. Sand, Ottawa, MCB, kiln-dried, 30-40 mesh. Sand should be acid-washed (steeped in *aqua regia* (ACS grades HNO<sub>3</sub>:HCl, 1:3, v:v) overnight, then washed three times each with H<sub>2</sub>O, CH<sub>3</sub>OH and CH<sub>2</sub>Cl<sub>2</sub>, dried, and stored at 120° C.
13. Sephadex LH-20, size-exclusion gel. Sephadex LH-20 should be swelled overnight in 6:4:3 solvent.
14. Silica gel, Davison Type 923 or Amicon No. 84080. Silica should be activated at 700° C for 18 hr, stored at 170° C, and cooled to room temperature in a desiccator just before weighing and use.
15. Sodium sulfate, reagent grade, anhydrous granular (Na<sub>2</sub>SO<sub>4</sub>). Sodium sulfate should be CH<sub>2</sub>Cl<sub>2</sub> washed, dried, stored at 120° C, and cooled to room temperature in a desiccator before weighing and use.
16. PCB/pesticide standard stock solution (100 µg/mL). From commercially available neat PCB and pesticide standards, weigh

1.00 mg of each congener and pesticide and dissolve 5 mL hexane. Dilute to 10.0 mL with hexane.

**NOTE:** PCB congener standards may also be purchased commercially at concentrations of 100 µg/mL.

17. PCB/pesticide primary dilution standard solution (1 µg/mL). Accurately measure a 100 µL aliquot of the PCB and pesticide standard stock solution and dilute to 10.0 mL of hexane.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Since field-moist samples are used in the determination, preservation of the sample is not practical. Therefore, analysis should begin as soon as possible after sample collection. A holding time of 7 days until extraction and 40 days from extraction to analysis is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C).

**NOTE:** Samples can be frozen to extend the holding time for up to 1 year.

All sample containers must be prewashed with detergents, acids, and Type II water. Glass containers should be used for the storage of samples to be analyzed for PCBs in sediments. All glassware and materials contacting the solvents should be washed with CH<sub>2</sub>Cl<sub>2</sub> three times prior to use.

An option to the CH<sub>2</sub>Cl<sub>2</sub> washing of the glassware is to combust the glassware in a muffle oven at 400° C for 4 hours.

## 7.0 Calibration and Standardization

### 7.1 General

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^\circ \text{C}$ .

The water bath and Kontes tube heater should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^\circ \text{C}$ .

### 7.2 Sephadex LH-20 Column Calibration

Information on preparing the Sephadex LH-20 column is presented in Attachment A.

1. Add enough azulene (approximately 10 mg/mL) and perylene (approximately 1 mg/mL) to approximately 50 mL of 6:4:3 solvent to produce a deeply colored solution.

**NOTE:** Make sure that the azulene and perylene are completely dissolved.

2. Place a 100 mL cylinder beneath the column and using a transfer pipet, cautiously remove any excess 6:4:3 solvent from the top of the packing.
3. Using a transfer pipet, cautiously apply 2 mL of the azulene/perylene calibration solution onto the column. Use a circular motion to dispense the solution just above the packing, and drip the solution slowly down the column wall so as not to disturb the packing.
4. Open the stopcock, drain to the packing top, and close the stopcock.
5. Add approximately 0.5 mL of solvent to the top of the column. Drain to the packing top, and close the stopcock.
6. Repeat step 5 once.

7. Add 100 mL of solvent, and open the stopcock.
8. Elute the solvent until all of the perylene has emerged, using the UV light to monitor the perylene. Record the volumes at which the azulene and perylene start and finish eluting.
9. If the azulene emerges in the 50-65 mL range, and the perylene emerges in the 60-80 mL range without distinct tailing on the packing, proceed to step 10. Otherwise, recycle the packing (Attachment A).
10. Discard the eluate. Add 50 mL of solvent to the column, and flush the packing by eluting 50 mL into the cylinder. Again, discard the eluate.
11. The column is now ready for the next sample.

**NOTE:** If the column is to be stored, maintain 30-50 mL of solvent in the column reservoir, and cover the top with aluminum foil. Remove the solvent if it separates into 2 phases, add 80 mL of fresh 6:4:3 solvent, and elute 50 mL.

### 7.3 GC Calibration

Calibration standards at a minimum of five concentration levels should be prepared. One of the calibration standards should be at a concentration near, but above, the method detection limit; the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in Tables 2 and 3 may be included). All initial calibration standards should be stored at -10° C to -20° C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The daily calibration standard (ongoing calibration should be prepared weekly and stored at 4° C.

Using the PCB/pesticide primary dilution standard solution, prepare the following suggested standards in 10 mL volumetric flasks:

<u>Primary Dilution Standard Solution (µL)</u>	<u>Concentration (µg/L)</u>
50	5
200	20
400	40
800	80
2000	200

Each standard should be brought to volume with hexane.

Linearity of the GC is determined by calculation of the individual response factors (RF) for each standard concentration using the following formula:

$$\text{RF} = \text{total peak area/mass of injected analyte.}$$

The calibration curve will be considered linear if the %RSD is  $\leq 30\%$  for each compound.

## 8.0 Procedure

### 8.1 Sediment Extraction

1. Decant the excess water from the sediment.

**NOTE:** Discard all extraneous materials. However, wood chip layers are common in Great Lakes sediments and may be an important part of the sample. If so, depending upon the project needs, the wood chips may be part of the sample.

2. Using a spatula and powder funnel, weigh a  $10 \pm .5$  g aliquot of the homogenized, field-moist sediment to the nearest 0.01 g into a tared bottle.
3. Centrifuge each sample bottle at  $<1500$  rpm for 5 min. Decant and discard the  $\text{H}_2\text{O}$ .
4. To each sediment sample, add 100 mL of  $\text{CH}_2\text{Cl}_2$ .
5. Add all surrogate spike solutions (see section 9.8).

**NOTE:** Make certain that the solutions are placed into the  $\text{CH}_2\text{Cl}_2$ .

6. Add 50 g of  $\text{Na}_2\text{SO}_4$ .
7. Clean bottle lip and threads to remove all sediment particles. Cap the bottle.

**NOTE:** Do not over tighten so as deform the cap and cause leakage.

8. Put Teflon™ tape around outside of cap and bottle.
9. Manually shake each bottle until the contents are loose.

10. Roll for approximately 16 hr (i.e., overnight) on the tumbler at 100-250 rpm.
11. Remove the tape from each bottle and decant the extract into a labeled flask.

**NOTE:** If the sample does not immediately settle, centrifuge at  $\leq 1500$  rpm for 5 min.

12. Add 100 mL of  $\text{CH}_2\text{Cl}_2$  to each sample, and repeat steps 6-9, except roll each bottle for 6 hr (i.e., during the day).
13. Decant the 2nd extract into the flask from step 10.
14. Repeat step 12, except roll each bottle for 16 hr (i.e., overnight).
15. Add the 3rd extract from step 13 to the flask from step 10.

## 8.2 Extract Concentration

1. Add 3-4 Teflon boiling chips to the flask containing the  $\text{CH}_2\text{Cl}_2$  extract from step 8.1 step 14, and attach a Snyder column.
2. Concentrate the extract in a  $60^\circ\text{C}$  water bath to 10-15 mL, and transfer concentrated extract to a labeled concentrator tube.
3. Wash down the flask with 3-4 mL of  $\text{CH}_2\text{Cl}_2$ , and add the washings to the tube.
4. Repeat step 3 once.
5. Add one boiling chip to the tube, and using the tube heater, concentrate the extract to between 0.9 and 1.0 mL.
6. Add 3 mL of hexane to the tube, and concentrate the extract to 2 mL using the tube heater.

## 8.3 Silica Gel/Alumina Chromatography

**NOTE:** The laboratory temperature must be  $<80^\circ\text{F}$  ( $27^\circ\text{C}$ ). On warm days proceed more slowly to avoid vapor bubbles.

**NOTE:** Columns should be prepared just prior to use.

1. Add 100 mL of  $\text{CH}_2\text{Cl}_2$  and between 5 and 15 mm glass wool plug to a 19 mm ID column with a stopcock. Tamp the plug well to remove any bubbles.

2. Add the 10 g alumina to a beaker and slowly add 20 mL of  $\text{CH}_2\text{Cl}_2$ . Gently swirl the beaker for 30 sec, and let it stand for 5 min (to remove all air bubbles).
3. Add the 20 g silica gel to a 2nd beaker. Slowly add 40 mL of  $\text{CH}_2\text{Cl}_2$  to the beaker. Gently swirl the beaker for 30 sec, and let it stand for 5 min (to remove all air bubbles).
4. Place a curved-stem funnel into the column reservoir so that the funnel tip hangs well off-center. Swirl the beaker to resuspend the alumina from step 2, and pour the slurry into the column.
5. Wash the beaker with approximately 5 mL of  $\text{CH}_2\text{Cl}_2$ , and add the washings to the column. Repeat the wash twice.
6. After the particles settle, open the stopcock for 30 sec to allow the alumina to pack more tightly, then close the stopcock.

**NOTE:** Gentle tapping of the column while the stopcock is open will assist in the settling of the alumina and silica gel.

7. Add the silica gel from step 3 to the column, as in steps 4 and 5.
8. After the particles settle, open the stopcock. While the solvent still drains, add 1 mL of sand through the powder funnel.
9. Drain  $\text{CH}_2\text{Cl}_2$  to the packing top, then close the stopcock.
10. Add 30 mL of 1:1  $\text{CH}_2\text{Cl}_2$ :pentane to the column. Drain to the packing top, then close the stopcock. Discard the eluates.
11. With a transfer pipet, cautiously transfer the sediment extract to the top of the packing. Drain to the packing top, then close the stopcock.
12. Wash down the sediment extract tube with 0.5 mL of 1:1  $\text{CH}_2\text{Cl}_2$ :pentane, and add the washings to the top of the packing. Drain to the packing top, then close the stopcock.
13. Repeat step 12 three times.
14. Add 200 mL of 1:1  $\text{CH}_2\text{Cl}_2$ :pentane, and continue eluting at approximately 3 mL/min.
15. Collect 20 mL of eluate, then close the stopcock, and discard the contents of the cylinder.
16. Replace the cylinder with a labeled flask and collect eluate until the column runs dry.

#### 8.4 Concentration of Extract

1. Add 3-4 boiling chips and a few grains of activated copper to the flask from step 15, section 8.3 until no further discoloring of the copper occurs.

**NOTE:** Activated copper is added to the flask to remove elemental sulfur, a potential interferant for GC/ECD analyses.

2. Attach a Snyder column and concentrate the fraction in a 60° C water bath to 10-15 mL, and transfer it to a concentrator tube.

**NOTE:** It is necessary to wet the Snyder column by adding CH<sub>2</sub>Cl<sub>2</sub> to the top of the column prior to sample boiling.

3. Wash down the flask with 3-4 mL of CH<sub>2</sub>Cl<sub>2</sub>, and add the washings to the tube.
4. Repeat step 3 once.
5. Add one boiling chip to the tube and concentrate the fraction to between 0.9 and 1.0 mL.
6. Add 2 mL of hexane to the tube and concentrate to between 0.9 and 1.0 mL.
7. Add approximately 0.7 mL of CH<sub>3</sub>OH and 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub>.

**NOTE:** This step results in a final solution ratio of 6:4:3 hexane:CH<sub>3</sub>OH:CH<sub>2</sub>Cl<sub>2</sub> (v:v:v).

**NOTE:** The extract must be dissolved in the solvent (no layers), with the total volume ≤ 2.3 mL.

## 8.5 Sephadex LH-20 Chromatography

**NOTE:** It is important to check column calibration on a monthly basis.

**NOTE:** During column storage, maintain 30-50 mL of the solvent in the column reservoir and cover the top with aluminum foil to minimize evaporation. If the solvent in the reservoir separates into 2 phases, remove it and replace it with >80 mL of fresh 6:4:3 solvent, then elute 50 mL.

1. Remove the excess solvent from the top of the column using a transfer pipet.

2. Add 10 mL of the 6:4:3 solvent to the column. Drain to the packing top, and close the stopcock. Discard the eluate.
3. Wash the column top with 2 mL of  $\text{CH}_2\text{Cl}_2$ , and place the 50-mL cylinder under the column.
4. Using a transfer pipet, carefully apply the extract from step 7, section 8.4 to the column.
5. Use a circular motion to dispense the sample immediately above the packing, dripping it slowly down the column wall so as not to disturb the packing.
6. Drain to the packing top, and close the stopcock.
7. Wash down the tube with 0.5 mL of 6:4:3 solvent, and apply the washings to the column. Drain to the packing top, and close the stopcock.
8. Repeat step 7 once.
9. Wash down the column wall with approximately 3 mL of 6:4:3 solvent, applied above the base of the reservoir. Drain to the packing top, and close the stopcock.
10. Repeat step 9 once.
11. Cautiously add approximately 150 mL of 6:4:3 solvent to the column without disturbing the packing.
12. Collect 25 mL of eluate in the 50 mL cylinder. Close the stopcock, and discard this eluate.
13. Replace the cylinder with a concentrator tube. Open the stopcock, collect approximately 15 to 20 mL of eluate (the amount calibrated in Section 7.2 steps 8 and 9 from just before where azulene first emerges from the column), then close the stopcock.
14. Archive this fraction.

**NOTE:** This fraction is archived in case early eluting compounds are not identified in the next fraction. If early eluting compounds are not identified in the next fraction, analyze the archived fraction for these compounds. If the compounds are identified in the archived fraction, a re-calibration of the Sephadex LH-20 column is necessary.

15. Place a 100 mL cylinder under the column. Open the stopcock, and collect approximately 50 to 55 mL of eluate (the amount calibrated in Section 7.2, steps 8 and 9 from 5 mL after the last perylene has eluted). Close the stopcock, and transfer the eluate to a flask.

16. Wash down the cylinder with 3 to 4 mL of  $\text{CH}_2\text{Cl}_2$ , and add the washings to the flask.
17. Repeat step 16 once.
18. Replace the 100 mL cylinder with a waste cylinder, and elute to the top of the packing. Discard this eluate. Add 50 mL of solvent and cap. The column is now ready for the next sample.

## 8.6 Concentration of Sephadex LH-20 Fraction

1. Add 3-4 boiling chips to the flask from step 17 section 8.5, and attach a Snyder column.

**NOTE:** It is necessary to wet the Snyder column by adding  $\text{CH}_2\text{Cl}_2$  to the top of the column prior to sample boiling.

2. Concentrate the fraction in a 75° C water bath to 10-15 mL, and transfer it to a concentrator tube.
3. Wash down the flask with 3-4 mL of  $\text{CH}_2\text{Cl}_2$ , and add the washings to the tube.
4. Repeat step 3 once.
5. Add one boiling chip to the tube and concentrate the fraction to between 0.9 and 1.0 mL.
6. Add 7 mL of hexane to the tube and concentrate to between 0.9 and 1.0 mL.

## 8.7 GC/ECD Analysis

The analyst should follow the instructions provided by the instrument's manufacturer for GC operation and maintenance. The following machine operating conditions are required for the proper determination and separation of the PCB congeners and pesticides:

### Machine Operating Conditions

Helium carrier	1.2 mL/min
Initial oven temperature	100° C
Initial hold time	1 min
First ramp rate	5°/min
First ramp final temperature	140°
Second hold time	1 min

Second ramp rate	1.5°/min
Second ramp final temperature	250° C
Third hold time	1 min
Third ramp rate	10°/min
Final temperature	300° C
Final hold time	5 min
ECD temperature	325° C
Injector port temperature	275° C

The primary quantification column should be a DB-5 0.25 mm ID column with a 30 m length. The secondary confirmation column should be a DB-17HT 0.25 mm ID column with a 30 m length.

When a PCB congener or pesticide is identified on the quantification column, the chromatogram of the confirmation column should also be checked to verify the identification of the analyte. If, however, the area of the confirmation column is lower than that of the quantification column, the area of the analyte in the confirmation column should be used to calculate the concentration of the analyte (along with the areas of the surrogates from the confirmation column).

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit.

The method detection limit for PCBs in sediments is 1 µg/kg per congener.

The method detection limits for pesticides in sediments are 10 µg/kg per compound.

**NOTE:** Method detection limits can be lowered by extracting larger amounts of sediments or by further concentrating the final extract volume (<1 mL).

## 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 25 percent or less between the measured total PCB or pesticide concentrations.

## 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 30\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

## 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a routine sediment sample collected and homogenized in bulk that has undergone multiple analyses by the analytical laboratory. Alternately, a LCS can be created by spiking a known quantity of the contaminant(s) of concern into a clean sediment, homogenizing the bulk sample, followed by multiple analyses at the analytical laboratory. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

## 9.5 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the

ongoing calibration check sample should be  $\pm 30\%$  of the mean RF from the initial calibration curve.

## 9.7 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - PCBs or pesticides, to the 10 g aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 30\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have a relative percent difference (RPD) of  $\leq 25\%$ .

## 9.8 Surrogate Spikes

A surrogate spike is defined as the addition of an organic compound which is similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in the environmental sample (USEPA, 1986). These compounds are spiked into all blanks, standards, samples, and spiked samples prior to extraction. Surrogate spikes should be spiked at between 50 and 100 times the method detection limit. Surrogate spike recoveries should be  $\pm 30\%$  of the known spiking concentration.

The following surrogate spike compounds are recommended:

- 4,4'-dibromooctafluorobiphenyl (DBOFB)
- decachlorobiphenyl (DCB)
- PCB congener 103
- PCB congener 198

## 9.9 Internal Standards

An internal standard (also known as GC standard) is added immediately prior to analysis by GC. The compound(s) added are sensitive to the detector and are a measure of analyte recovery without (or with highly reduced) matrix effects. These compounds are spiked into all blanks, standards, samples, and spiked samples. Internal standards should be spiked at between 50 and 100

times the method detection limit. Internal standard recoveries should be  $\pm 30\%$  of the known concentration. The recommended internal standard for this method is tetrachloro-m-xylene (TCMX).

Control charts for the internal standards, with  $\pm 2$  and  $3 \sigma$  values as warning and action limits, respectively, will be required to be created and updated after each day of analysis to control any systematic bias that may be adding to the overall measurement uncertainty for a given parameter. A value outside the control limits is considered unacceptable, hence, the instrument should be recalibrated and the samples in that batch should be reanalyzed. If bias for a given analysis is indicated, i.e., at least seven successive points occurring on one side of the cumulative means, sample analysis should cease until an explanation is found and the system is brought under control.

## 10.0 Method Performance

Precision and accuracy information are not available at this time.

## 11.0 Calculations and Reporting

Identify the analyte peaks in the chromatograms of the extract fractions by comparing them with the analyte retention times obtained from the chromatogram of the ongoing calibration standard.

**NOTE:** When a PCB congener or pesticide is identified on the quantification column, the chromatogram of the confirmation column should also be checked to verify the identification of the analyte. If, however, the area of the confirmation column is lower than that of the quantification column, the area of the analyte in the confirmation column should be used to calculate the concentration of the analyte (along with the areas of the surrogates from the confirmation column).

The concentration of an analyte in the sediment sample, dry weight basis:

$$\text{PCB/pesticide, ng/g (dry weight)} = \frac{R_1 \times R_2 \times ss \times 100}{R_3 \times g \times dw}$$

where:

$$R_1 = \frac{\text{analyte peak area from the sample}}{\text{surrogate spike peak area from the sample}}$$

$R_2$  = analyte concentration in the ongoing calibration standard (ng/μL)  
surrogate spike concentration in the ongoing calibration  
standard (ng/μL)

$R_3$  = analyte peak area from the ongoing calibration standard  
surrogate spike peak area from the ongoing calibration standard

ss = surrogate spike concentration added to sample (ng)

g = wet weight of sediment sample, g

dw = % dry weight of sample determined from total solids analysis

The concentration of the total PCBs in the sediment sample is calculated by summation of the 20 congeners (Table 3) as follows:

Total PCBs, ng/g (dry weight) =  $\Sigma$  congener concentrations

**If the congener concentration is < method detection limit, then a "0" value should be used during summation (i.e., do not add the method detection limit for non-identified congeners).**

**NOTE:** The USEPA/USACE Task Group that developed the Great Lakes Dredged Material Testing & Evaluation Manual never intended that regulatory decisions should be made by the comparison of concentrations of individual congeners. The summation of congeners should be the only value reported, unless the values of individual congeners summed is explicitly requested.

## 12.0 References

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## Attachment A - Sephadex LH-20 Column Packing and Recycling

### A.1 Column Packing

1. Fit a 19 mm ID column with a stopcock, add 10 mL of 6:4:3 solvent and between 5 and 10 mm glass wool plug. Tamp the plug to remove any air bubbles.
2. Add approximately 1 mL of sand to the column, and tap the column gently so that the sand forms a smooth layer on top of the glass wool.
3. Pour the swelled Sephadex gel through the funnel into the column until the gel fills the column and about 1/4 of the reservoir.
4. Allow 10 min for the Sephadex to settle. Open the stopcock, and elute 80 mL of solvent to ensure firm packing. Add more solvent as needed. Leave 30 mL of solvent in the column reservoir. Cover the top with aluminum foil, and allow the packing to settle overnight.
5. Open the stopcock, and elute 10 mL of solvent, then close the stopcock. Remove the excess Sephadex packing from the top with a transfer pipet until the height of the Sephadex is 26.5 cm.
6. Gently add approximately 1 mL of sand onto the packing so that it forms an even layer on the top. (The column may be tapped or tilted slightly to get an even layer of sand.)
7. Examine the packing for air bubbles. If bubbles are evident, elute approximately 250 mL of warm (about 35° C) solvent through the column. If the bubbles persist, recycle the packing (see section A.2).

### A.2 Recycling Sephadex LH-20 Column Packing

**NOTE:** When the column no longer maintains its calibration with azulene/perylene, recycle the packing.

1. Decant any solvent in the column reservoir.
2. Empty the column packing into a beaker 4 times the volume of the packing.
3. Wash with  $\text{CH}_2\text{Cl}_2$ .
4. Add enough  $\text{CH}_2\text{Cl}_2$  to float Sephadex particles in the upper half of the beaker.
5. Remove all glass wool with forceps (mandatory).
6. Cover the beaker and let stand for 1 to 2 hours.
7. Decant the floating particles leaving the sand in the beaker.
8. Aspirate the  $\text{CH}_2\text{Cl}_2$  from the Sephadex particles and set them aside.
9. Swell these particles overnight in 6:4:3 solvent before reusing.

# POLYNUCLEAR AROMATIC HYDROCARBONS IN SEDIMENTS (GC/MS, CAPILLARY COLUMN)

## 1.0 Scope and Application

This method is appropriate for the determination of polynuclear aromatic hydrocarbons (PAHs) in sediment samples. Individual polynuclear aromatic compounds that are soluble in methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) and capable of being eluted without derivitization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone are listed in Table 1.

This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

Extraction and quantification techniques are based on SW-846 Method 8270 (USEPA, 1986). The extract clean-up procedures are based on a National Oceanic and Atmospheric Administration (NOAA) method for the determination of Extractable Toxic Organic Compounds in marine sediments (NOAA, 1985).

The extracts produced from this method (sections 8.1 through 8.6) can be used in the determination of polychlorinated biphenyls (PCBs), pesticides, and PAHs.

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" sediments. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

The sample is extracted with methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) and sodium sulfate ( $\text{Na}_2\text{SO}_4$ ). The resultant extract is cleaned-up with silica gel and alumina. Additional clean-up steps to remove biological macromolecules are performed using Sephadex LH-20. The final sample extract is injected into a gas chromatograph/mass spectrometer system using a capillary column for

separation, identification, and quantification of the individual PAHs present in the sample.

The same extract used to analyze for PAHs can be used to analyze for PCBs and pesticides using gas chromatography with electron capture detection (GC/ECD). The method for PCB and pesticide determination is provided in this methods manual.

### 3.0 Interferences

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences during the analysis of samples. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing reagent blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.001 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Centrifuge, capable of holding 250 mL centrifuge tubes and maintaining speeds of 1500 rpm.
4. Desiccator and desiccant. Desiccants generally used include: anhydrous calcium sulfate, silica gel, or phosphorus pentoxide. Indicating desiccants are preferable since they show when the desiccant needs to be changed or regenerated.
5. Gas chromatograph/mass spectrometer system with:
  - a. gas chromatograph system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes,

- analytical columns, and gases. The capillary column should be directly coupled to the source.
- b. mass spectrometer capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode.
  - c. GC/MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used.
  - d. data system: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should also be available.
6. Modified Kontes tube heater (block contains: Al inserts fitted to the 0.7 mL line of the tube tip and an Al-foil shroud).
  7. Molecular sieve traps (for gas cylinder)

**NOTE:** One suggested source for the molecular sieve traps is Hydro-Purge model ASC-I, Coast Engineering Laboratory, Gardena, California.

8. Oxygen traps.
9. UV light source.
10. Water bath, capable of maintaining a temperature of  $80 \pm 2^\circ \text{C}$ .

**NOTE:** The bath should be used in a hood.

## 4.2 Materials

1. Beakers, 250 mL, or equivalent.
2. Centrifuge tubes, 250 mL, amber, with Teflon™ caps.

- cm.
3. Chromatography column with reservoir 250 mL, 19 mm ID, 30
  4. Erlenmeyer flask, 500 mL, with stopper.
  5. Erlenmeyer flask, 1 L, with stopper.
  6. Funnel, curved-stem (curve must be glassblown).
  7. Funnel, 200 mm OD, long-stem.
  8. Funnel, powder.
  9. GC column, silicon-coated fused-silica capillary column, DB-5, 30 m x 0.25 mm I.D. (or 0.32 mm I.D.).
  10. Graduated cylinder, 500 mL.
  11. Graduated cylinder, 100 mL.
  12. Graduated cylinder, 50 mL.
  13. Kontes concentrator tube, 25 mL, with stopper.
  14. Kuderna-Danish concentrator tube, 10 mL, graduated.
  15. Kuderna-Danish evaporative flask, 500 mL.
  16. pH paper, wide range, capable of determining pH from 4 to 10.
  17. Separatory funnel, 2 L, with Teflon™ stopcock.
  18. Snyder column, 3-ball macro.
  19. Syringe, 2000 µL.
  20. Syringe, 800 µL.
  21. Syringe, 400 µL.
  22. Syringe, 200 µL.
  23. Syringe, 100 µL.
  24. Syringe, 50 µL.
  25. Syringe, 10 µL.
  26. Teflon wash-bottle, 500 mL (to be filled with CH<sub>2</sub>Cl<sub>2</sub>).
  27. Transfer pipets (Pasteur style) with rubber bulbs.
  28. GC vials, 2 mL.
  29. GC vials, 100 µL, conical.
  30. Volumetric flask, class A, 100 mL
  31. Volumetric flask, class A, 50 mL
  32. Volumetric flask, class A, 10 mL
  33. Volumetric pipet, 50 mL.

## 5.0 Reagents

1. Alumina, 80-200 mesh. Alumina should be activated at 120° C for 2 hr and then cooled to room temperature in a desiccator just before weighing and use.

2. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
3. Azulene, reagent grade (C<sub>15</sub>H<sub>18</sub>).
4. Copper, reagent grade, fine granular. Copper should be activated < 1 hr before use. To activate copper, cover with concentrated HCl and stir with a glass rod. Allow to stand for 5 min followed by washing twice with CH<sub>3</sub>OH and then 3 times with CH<sub>2</sub>Cl<sub>2</sub>. Leave copper covered with CH<sub>2</sub>Cl<sub>2</sub> to avoid contact with air.
5. Helium, grade 4.5 (purified, ≥99.995 %).
6. Hexane, high purity (C<sub>6</sub>H<sub>14</sub>). Each solvent lot should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the solvent has a concentration <MDL, then the solvent can be used.
7. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
8. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
9. Methanol, high purity (CH<sub>3</sub>OH). Each solvent lot should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the solvent has a concentration <MDL, then the solvent can be used.
10. Methylene chloride (dichloromethane), high purity (CH<sub>2</sub>Cl<sub>2</sub>). Each solvent lot should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the solvent has a concentration <MDL, then the solvent can be used.
11. Pentane, high purity (C<sub>5</sub>H<sub>12</sub>). Each solvent lot should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the solvent has a concentration <MDL, then the solvent can be used.
12. Perylene, reagent grade (C<sub>20</sub>H<sub>12</sub>).
13. Sand, Ottawa, MCB, kiln-dried, 30-40 mesh. Sand should be acid-washed (steeped in *aqua regia* (ACS grades HNO<sub>3</sub>:HCl, 1:3, v:v) overnight, then washed three times each with Type II H<sub>2</sub>O, CH<sub>3</sub>OH and CH<sub>2</sub>Cl<sub>2</sub>, dried, and stored at 120° C.

14. Sephadex LH-20, size-exclusion gel. Sephadex LH-20 should be swelled overnight in 6:4:3 solvent.
15. Silica gel, Davison Type 923 or Amicon No. 84080. Silica should be activated at 700° C for 18 hr, stored at 170° C, and cooled to room temperature in a desiccator just before weighing and use.
16. Sodium hydroxide, 10 N (NaOH). Add 20 g of NaOH to 400 mL Type II water. Dilute to 500 mL with Type II water.
17. Sodium sulfate, reagent grade, anhydrous granular (Na<sub>2</sub>SO<sub>4</sub>). Sodium sulfate should be CH<sub>2</sub>Cl<sub>2</sub> washed, dried, stored at 120° C, and cooled to room temperature in a desiccator before weighing and use.
18. PAH standard stock solution (1.00 µg/µL). PAH stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

**NOTE:** Prepare stock standard solutions by accurately weighing 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4° C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

Stock standard solutions must be replaced after 1 yr, or sooner, if comparison with quality control check samples indicates a problem.

19. GC/MS tuning standard. A methylene chloride solution containing 50 ng/µL of decafluorotriphenylphosphine (DFTPP) should be prepared. Store at 4° C or less when not being used.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Sample containers should be filled with care so as to prevent contamination due to any portion of the collected sample coming in contact with the sampler's gloves.

Samples should not be collected or stored in the presence of exhaust fumes.

Since field-moist samples are used in the determination, preservation of the sample is not practical. Therefore, analysis should begin as soon as possible after sample collection. A holding time of 7 days until extraction and 40 days from extraction to analysis is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C) in the dark.

**NOTE:** Samples can be frozen to extend the holding time for up to 1 year.

All sample containers must be prewashed with detergents, acids, and Type II water. Glass containers should be used for the storage of samples to be analyzed for PAHs in sediments. All glassware and materials contacting the solvents should be washed with CH<sub>2</sub>Cl<sub>2</sub> three times prior to use.

An option to the CH<sub>2</sub>Cl<sub>2</sub> washing of the glassware is to combust the glassware in a muffle oven at 400° C for 4 hours.

## 7.0 Calibration and Standardization

### 7.1 General

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^\circ \text{C}$ .

The water bath and Kontes tube heater should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^\circ \text{C}$ .

### 7.2 Sephadex LH-20 Column Calibration

Information on preparing the Sephadex LH-20 column is presented in Attachment A.

1. Add enough azulene (approximately 10 mg/mL) and perylene (approximately 1 mg/mL) to approximately 50 mL of 6:4:3 solvent to produce a deeply colored solution.

**NOTE:** Make sure that the azulene and perylene are completely dissolved.

2. Place a 100 mL cylinder beneath the column and using a transfer pipet, cautiously remove any excess 6:4:3 solvent from the top of the packing.
3. Using a transfer pipet, cautiously apply 2 mL of the azulene/perylene calibration solution onto the column. Use a circular motion to dispense the solution just above the packing, and drip the solution slowly down the column wall so as not to disturb the packing.
4. Open the stopcock, drain to the packing top, and close the stopcock.
5. Add approximately 0.5 mL of solvent to the top of the column. Drain to the packing top, and close the stopcock.
6. Repeat step 5 once.

7. Add 100 mL of solvent, and open the stopcock.
8. Elute the solvent until all of the perylene has emerged, using the UV light to monitor the perylene. Record the volumes at which the azulene and perylene start and finish eluting.
9. If the azulene emerges in the 50-65 mL range, and the perylene emerges in the 60-80 mL range without distinct tailing on the packing, proceed to step 10. Otherwise, recycle the packing (Attachment A).
10. Discard the eluate. Add 50 mL of solvent to the column, and flush the packing by eluting 50 mL into the cylinder. Again, discard the eluate.
11. The column is now ready for the next sample.

**NOTE:** If the column is to be stored, maintain 30-50 mL of solvent in the column reservoir, and cover the top with aluminum foil. Remove the solvent if it separates into 2 phases, add 80 mL of fresh 6:4:3 solvent, and elute 50 mL.

### 7.3 GC Calibration

Calibration standards at a minimum of five concentration levels should be prepared. One of the calibration standards should be at a concentration near, but above, the method detection limit; the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method. All initial calibration standards should be stored at  $-10^{\circ}$  to  $-20^{\circ}$  C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The daily calibration standard (ongoing calibration standard) should be prepared weekly and stored at  $4^{\circ}$  C.

Each GC/MS system must be hardware-tuned to meet the criteria in Table 2 for the GC/MS tuning standard. Analyses should not begin until all these criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. If chromatogram peak degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6 to 12 in. of the capillary column.

Analyze each calibration standard (1 µL containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (Table 1). Calculate response factors (RFs) for each compound as follows:

$$RF = (A_x C_{is}) / (A_{is} C_x)$$

where:

$A_x$  = area of the characteristic ion for the compound being measured.

$A_{is}$  = area of the characteristic ion for the specific internal standard.

$C_x$  = concentration of the compound being measured (ng/µL).

$C_{is}$  = concentration of the specific internal standard (ng/µL).

The average RF should be calculated for each compound. The percent relative standard deviation (%RSD) should also be calculated for each compound. The %RSD should be less than 30% for each compound. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units.

**NOTE:** Late eluting compounds usually have much better agreement.

## 8.0 Procedure

### 8.1 Sediment Extraction

1. Decant the excess water from the sediment.

**NOTE:** Discard all extraneous materials. However, wood chip layers are common in Great Lakes sediments and may be an important part of the sample. If so, depending upon the project needs, the wood chips may be part of the sample.

2. Using a spatula and powder funnel, weigh a  $10 \pm .5$  g aliquot of the homogenized, field-moist sediment to the nearest 0.01 g into a tared bottle.
3. Centrifuge each sample bottle at <1500 rpm for 5 min. Decant and discard the H<sub>2</sub>O.
4. To each sediment sample, add 100 mL of CH<sub>2</sub>Cl<sub>2</sub>.

**NOTE:** Be sure to add all surrogate spike solutions at this point. Make certain that the solutions are placed into the  $\text{CH}_2\text{Cl}_2$ .

5. Add 50 g of  $\text{Na}_2\text{SO}_4$ .
6. Clean bottle lip and threads to remove all sediment particles. Cap the bottle.

**NOTE:** Do not over tighten so as deform the cap and cause leakage.

7. Put Teflon<sup>™</sup> tape around outside of cap and bottle.
8. Manually shake each bottle until the contents are loose.
9. Roll for approximately 16 hr (i.e., overnight) on the tumbler at 100-250 rpm.
10. Remove the tape from each bottle and decant the extract into a labeled flask.

**NOTE:** If the sample does not immediately settle, centrifuge at  $\leq 1500$  rpm for 5 min.

11. Add 100 mL of  $\text{CH}_2\text{Cl}_2$  to each sample, and repeat steps 6-9, except roll each bottle for 6 hr (i.e., during the day).
12. Decant the 2nd extract into the flask from step 10.
13. Repeat step 12, except roll each bottle for 16 hr (i.e., overnight).
14. Add the 3rd extract from step 13 to the flask from step 10.

## 8.2 Extract Concentration

1. Add 3-4 Teflon boiling chips to the flask containing the  $\text{CH}_2\text{Cl}_2$  extract from step 8.1 step 14, and attach a Snyder column.
2. Concentrate the extract in a  $60^\circ\text{C}$  water bath to 10-15 mL, and transfer concentrated extract to a labeled concentrator tube.
3. Wash down the flask with 3-4 mL of  $\text{CH}_2\text{Cl}_2$ , and add the washings to the tube.
4. Repeat step 3 once.
5. Add one boiling chip to the tube, and using the tube heater, concentrate the extract to between 0.9 and 1.0 mL.
6. Add 3 mL of hexane to the tube, and concentrate the extract to 2 mL using the tube heater.

### 8.3 Silica Gel/Alumina Chromatography

**NOTE:** The laboratory temperature must be  $<80^{\circ}\text{F}$  ( $27^{\circ}\text{C}$ ). On warm days proceed more slowly to avoid vapor bubbles.

**NOTE:** Columns should be prepared just prior to use.

1. Add 100 mL of  $\text{CH}_2\text{Cl}_2$  and between 5 and 15 mm glass wool plug to a 19 mm ID column with a stopcock. Tamp the plug well to remove any bubbles.
2. Add the 10 g alumina to a beaker and slowly add 20 mL of  $\text{CH}_2\text{Cl}_2$ . Gently swirl the beaker for 30 sec, and let it stand for 5 min (to remove all air bubbles).
3. Add the 20 g silica gel to a 2nd beaker. Slowly add 40 mL of  $\text{CH}_2\text{Cl}_2$  to the beaker. Gently swirl the beaker for 30 sec, and let it stand for 5 min (to remove all air bubbles).
4. Place a curved-stem funnel into the column reservoir so that the funnel tip hangs well off-center. Swirl the beaker to resuspend the alumina from step 2, and pour the slurry into the column.
5. Wash the beaker with approximately 5 mL of  $\text{CH}_2\text{Cl}_2$ , and add the washings to the column. Repeat the wash twice.
6. After the particles settle, open the stopcock for 30 sec to allow the alumina to pack more tightly, then close the stopcock.

**NOTE:** Gentle tapping of the column while the stopcock is open will assist in the settling of the alumina and silica gel.

7. Add the silica gel from step 3 to the column, as in steps 4 and 5.
8. After the particles settle, open the stopcock. While the solvent still drains, add 1 mL of sand through the powder funnel.
9. Drain  $\text{CH}_2\text{Cl}_2$  to the packing top, then close the stopcock.
10. Add 30 mL of 1:1  $\text{CH}_2\text{Cl}_2$ :pentane to the column. Drain to the packing top, then close the stopcock. Discard the eluates.
11. With a transfer pipet, cautiously transfer the extract to the top of the packing. Drain to the packing top, then close the stopcock.
12. Wash down the extract tube with 0.5 mL of 1:1  $\text{CH}_2\text{Cl}_2$ :pentane, and add the washings to the top of the packing. Drain to the packing top, then close the stopcock.
13. Repeat step 12 three times.
14. Add 200 mL of 1:1  $\text{CH}_2\text{Cl}_2$ :pentane, and continue eluting at approximately 3 mL/min.

15. Collect 20 mL of eluate, then close the stopcock, and discard the contents of the cylinder.
16. Replace the cylinder with a labeled flask and collect eluate until the column runs dry.

#### 8.4 Concentration of Extract

1. Add 3-4 boiling chips and a few grains of activated copper to the flask from step 15, section 8.3 until no further discoloring of the copper occurs.

**NOTE:** Activated copper is added to the flask to remove elemental sulfur, a potential interferant for GC/ECD analyses.

2. Attach a Snyder column and concentrate the fraction in a 60° C water bath to 10-15 mL, and transfer it to a concentrator tube.

**NOTE:** It is necessary to wet the Snyder column by adding CH<sub>2</sub>Cl<sub>2</sub> to the top of the column prior to sample boiling.

3. Wash down the flask with 3-4 mL of CH<sub>2</sub>Cl<sub>2</sub>, and add the washings to the tube.
4. Repeat step 3 once.
5. Add one boiling chip to the tube and concentrate the fraction to between 0.9 and 1.0 mL.
6. Add 2 mL of hexane to the tube and concentrate to between 0.9 and 1.0 mL.
7. Add approximately 0.7 mL of CH<sub>3</sub>OH and 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub>.

**NOTE:** This step results in a final solution ratio of 6:4:3 hexane:CH<sub>3</sub>OH:CH<sub>2</sub>Cl<sub>2</sub> (v:v:v).

**NOTE:** The extract must be dissolved in the solvent (no layers), with the total volume ≤ 2.3 mL.

#### 8.5 Sephadex LH-20 Chromatography

**NOTE:** It is important to check column calibration on a monthly basis.

**NOTE:** During column storage, maintain 30-50 mL of the solvent in the column reservoir and cover the top with aluminum foil to minimize evaporation. If the solvent in the reservoir separates into 2 phases, remove it and replace it with >80 mL of fresh 6:4:3 solvent, then elute 50 mL.

1. Remove the excess solvent from the top of the column using a transfer pipet.
2. Add 10 mL of the 6:4:3 solvent to the column. Drain to the packing top, and close the stopcock. Discard the eluate.
3. Wash the column top with 2 mL of  $\text{CH}_2\text{Cl}_2$ , and place the 50-mL cylinder under the column.
4. Using a transfer pipet, carefully apply the extract from step 7, section 8.4, to the column.
5. Use a circular motion to dispense the sample immediately above the packing, dripping it slowly down the column wall so as not to disturb the packing.
6. Drain to the packing top, and close the stopcock.
7. Wash down the tube with 0.5 mL of 6:4:3 solvent, and apply the washings to the column. Drain to the packing top, and close the stopcock.
8. Repeat step 7 once.
9. Wash down the column wall with approximately 3 mL of 6:4:3 solvent, applied above the base of the reservoir. Drain to the packing top, and close the stopcock.
10. Repeat step 9 once.
11. Cautiously add approximately 150 mL of 6:4:3 solvent to the column without disturbing the packing.
12. Collect 25 mL of eluate in the 50 mL cylinder. Close the stopcock, and discard this eluate.
13. Replace the cylinder with a concentrator tube. Open the stopcock, collect approximately 15 to 20 mL of eluate (the amount calibrated in Section 7.2 steps 8 and 9 from just before where azulene first emerges from the column), then close the stopcock.
14. Archive this fraction.

**NOTE:** This fraction is archived in case early eluting compounds are not identified in the next fraction. If early eluting compounds are not identified in the next fraction, analyze the archived fraction for these compounds. If the compounds are

identified in the archived fraction, a re-calibration of the Sephadex LH-20 column is necessary.

15. Place a 100 mL cylinder under the column. Open the stopcock, and collect approximately 50 to 55 mL of eluate (the amount calibrated in Section 7.2, steps 8 and 9 from 5 mL after the last perylene has eluted). Close the stopcock, and transfer the eluate to a flask.
16. Wash down the cylinder with 3 to 4 mL of  $\text{CH}_2\text{Cl}_2$ , and add the washings to the flask.
17. Repeat step 16 once.
18. Replace the 100 mL cylinder with a waste cylinder, and elute to the top of the packing. Discard this eluate. Add 50 mL of solvent and cap. The column is now ready for the next sample.

## 8.6 Concentration of Sephadex LH-20 Fraction

1. Add 3-4 boiling chips to the flask from step 17 section 8.5, and attach a Snyder column.

**NOTE:** It is necessary to wet the Snyder column by adding  $\text{CH}_2\text{Cl}_2$  to the top of the column prior to sample boiling.

2. Concentrate the fraction in a 75° C water bath to 10-15 mL, and transfer it to a concentrator tube.
3. Wash down the flask with 3-4 mL of  $\text{CH}_2\text{Cl}_2$ , and add the washings to the tube.
4. Repeat step 3 once.
5. Add one boiling chip to the tube and concentrate the fraction to between 0.9 and 1.0 mL.
6. Add 7 mL of hexane to the tube and concentrate to between 0.9 and 1.0 mL.

## 8.7 GC/MS Analysis

The analyst should follow the instructions provided by the instrument's manufacturer for GC operation and maintenance. The recommended GC/MS operating conditions for PAH quantification are:

Mass Range	35-500 amu
Scan time	1 sec/scan
Initial column temperature	40° C

Initial hold time:	4 min
Column temperature program	40-270° C at 10°C/min
Final column temperature hold	270° C (until benzo[g,h,i]perylene has eluted)
Injector temperature	250-300° C
Transfer line temperature	250-300° C
Source temperature	According to manufacturer's specifications
Injector	Grob-type, splitless
Sample volume	1-2 µL
Carrier gas	Helium at 30 cm/sec.

The primary quantification column should be a DB-5 0.25 mm I.D. column with a 30 m length.

The volume to be injected should ideally contain 100 ng of the PAHs (for a 1 µL injection).

**NOTE:** It is highly recommended that the extract be screened on a GC with flame ionization detection (FID) or GC with photoionization detection (PID) using the same type of capillary column (DB-5 0.25 mm I.D. with a 30 m length). This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit.

The method detection limit for PAHs in sediments is 50 µg/kg.

**NOTE:** Method detection limits can be lowered by extracting larger amounts of sediments or by further concentrating the final extract volume (<1 mL).

## 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 25 percent or less between the measured PAH concentrations.

## 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 30\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

## 9.4 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

One reagent blank should also be analyzed prior to any routine sample analyses to ensure interferences and contamination are under control.

## 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 30\%$  of the mean RF from the initial calibration curve.

## 9.6 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - PAHs, to the 1 L aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at

the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 30\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 30\%$ .

## 9.7 Surrogate Spikes

A surrogate spike is defined as the addition of an organic compound which is similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in the environmental sample (USEPA, 1986). These compounds are spiked into all blanks, standards, samples, and spiked samples prior to extraction. Surrogate spikes should be spiked at between 50 and 100 times the method detection limit. Surrogate spike recoveries should be  $\pm 30\%$  of the known spiking concentration.

The following surrogate spike compounds are recommended:

naphthalene-d<sub>8</sub>  
acenaphthene-d<sub>10</sub>  
perylene-d<sub>12</sub>

Other surrogate spike compounds that are also commonly used are phenanthrene-d<sub>10</sub> and chrysene-d<sub>12</sub>.

Control charts for the surrogate spikes, with  $\pm 2$  and  $3 \sigma$  values as warning and action limits, respectively, will be required to be created and updated after each day of analysis to control any systematic bias that may be adding to the overall measurement uncertainty for a given parameter. A value outside the control limits is considered unacceptable, hence, the instrument should be recalibrated and the samples in that batch should be reanalyzed. If bias for a given analysis is indicated, i.e., at least seven successive points occurring on one side of the cumulative means, sample analysis should cease until an explanation is found and the system is brought under control.

## 9.8 Internal Standards

An internal standard (also known as GC standard) is added immediately prior to analysis by GC. The compound(s) added are sensitive to the detector

and are a measure of analyte recovery without (or with highly reduced) matrix effects. These compounds are spiked into all blanks, standards, samples, and spiked samples. Internal standards should be spiked at between 50 and 100 times the method detection limit. Internal standard recoveries should be  $\pm 30\%$  of the known concentration. The recommended internal standard for this method is tetrachloro-m-xylene (TCMX). An alternate internal standard often used is hexamethylbenzene (HMB).

Control charts for the internal standards, with  $\pm 2$  and  $3\sigma$  values as warning and action limits, respectively, will be required to be created and updated after each day of analysis to control any systematic bias that may be adding to the overall measurement uncertainty for a given parameter. A value outside the control limits is considered unacceptable, hence, the instrument should be recalibrated and the samples in that batch should be reanalyzed. If bias for a given analysis is indicated, i.e., at least seven successive points occurring on one side of the cumulative means, sample analysis should cease until an explanation is found and the system is brought under control.

### 9.9 Ongoing GC/MS Tuning Standard

A 50 ng injection of the GC/MS tuning standard (DFTPP) must be made during each 12 hour shift. Acceptance criteria in the mass spectrum for DFTPP must meet the criteria given in Table 2.

## 10.0 Method Performance

Precision and accuracy information are not available at this time.

## 11.0 Calculations and Reporting

### 11.1 Qualitative Analysis

An analyte is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for the standard reference should be obtained on the GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as

the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

The sample component RRT must compare within  $\pm 0.06$  RRT units of the RRT of the standard component. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum. The relative intensities of ions must agree within plus or minus 20% between the standard and sample spectra (i.e., an ion with an abundance of 50% in the standard spectra must have the corresponding sample abundance between 30 and 70 percent).

For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Computer-generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

1. Relative intensities of major ions in the reference spectrum (ion >10% of the most abundant ion) should be present in the sample spectrum.
2. The relative intensities of the major ions should agree within  $\pm 20\%$ . (i.e., an ion with an abundance of 50% in the standard spectrum must have the corresponding sample ion abundance between 30 and 70%).
3. Molecular ions present in the reference spectrum should be present in sample the spectrum.
4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting

peaks. Data system library reduction programs can sometimes create these discrepancies.

## 11.2 Quantitative Analysis

When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte.

Calculate the concentration of each identified analyte in the sample as follows:

$$\text{PAH, } \mu\text{g/kg (dry weight)} = \frac{A_x \times I_s \times V_t}{A_{is} \times R_F \times V_i \times g \times dw}$$

where:

$A_x$  = area of characteristic ion for compound being measured.

$I_s$  = amount of internal standard injected (ng).

$V_t$  = volume of total extract ( $\mu\text{L}$ ).

$A_{is}$  = area of characteristic ion for the internal standard.

$R_F$  = response factor for compound being measured.

$V_i$  = volume of extract injected ( $\mu\text{L}$ ).

$g$  = wet weight of sediment sample, g.

$dw$  = % dry weight of sample determined from total solids analysis.

Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: the areas  $A_x$  and  $A_{is}$  should be from the total ion chromatograms and the  $R_F$  for the compound should be assumed to equal 1. The concentration obtained using this method should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

Report results without correction for recovery data in  $\mu\text{g/kg}$  of each PAH.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

J.W. Eichelberger, L.E. Harris, and W.L. Budde. 1975. Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry. *Anal. Chem.* 47:995.

National Oceanic and Atmospheric Administration. 1985. Standard Analytical Procedures of the NOAA National Analytical Facility 1985-1985: Extractable toxic organic compounds. 2nd ed. NOAA Tech. Memo. NMFS F/NWC-92.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Table 1. Characteristic Ions for PAHs.

Compound	Retention	
	Time (min)	Primary Ion Secondary Ion(s)
Acenaphthene	15.13	154 153, 152
Acenaphthene-d <sub>10</sub> (SS)	15.05	164 162, 160
Acenaphthylene	14.57	152 151, 153
Anthracene	19.77	178 176, 179
Benzo(a)anthracene	27.83	228 229, 226
Benzo(b)fluoranthene	31.45	252 253, 125
Benzo(k)fluoranthene	31.55	252 253, 125
Benzo(g,h,i)perylene	41.43	276 138, 277
Benzo(a)pyrene	32.80	252 253, 125
Chrysene	27.97	228 226, 229
Dibenz(a,h)anthracene	39.82	278 139, 279
Fluoranthene	23.33	202 101, 203
Fluorene	16.70	166 165, 167
Indeno(1,2,3-cd)pyrene	39.52	276 138, 227
2-Methylnaphthalene	11.87	142 141
Naphthalene-d <sub>8</sub> (SS)	9.75	136 68
Perylene-d <sub>12</sub> (SS)	33.05	264 260, 265
Phenanthrene	19.62	178 179, 176
Pyrene	24.02	202 200, 203
Tetrachloro-m-xylene (IS)		

IS = internal standard

SS = surrogate spike

<sup>a</sup>estimated retention times.

Table 2. DFTPP Key Ions and Ion Abundance Criteria<sup>a</sup>

<u>Mass</u>	<u>Ion Abundance Criteria</u>
51	30-60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30 of mass 198
365	>1% of mass 198
441	Present but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

a = from Eichelberger et al., 1975.

## Attachment A - Sephadex LH-20 Column Packing and Recycling

### A.1 Column Packing

1. Fit a 19 mm ID column with a stopcock, add 10 mL of 6:4:3 solvent and between 5 and 10 mm glass wool plug. Tamp the plug to remove any air bubbles.
2. Add approximately 1 mL of sand to the column, and tap the column gently so that the sand forms a smooth layer on top of the glass wool.
3. Pour the swelled Sephadex gel through the funnel into the column until the gel fills the column and about 1/4 of the reservoir.
4. Allow 10 min for the Sephadex to settle. Open the stopcock, and elute 80 mL of solvent to ensure firm packing. Add more solvent as needed. Leave 30 mL of solvent in the column reservoir. Cover the top with aluminum foil, and allow the packing to settle overnight.
5. Open the stopcock, and elute 10 mL of solvent, then close the stopcock. Remove the excess Sephadex packing from the top with a transfer pipet until the height of the Sephadex is 26.5 cm.
6. Gently add approximately 1 mL of sand onto the packing so that it forms an even layer on the top. (The column may be tapped or tilted slightly to get an even layer of sand.)
7. Examine the packing for air bubbles. If bubbles are evident, elute approximately 250 mL of warm (about 35° C) solvent through the column. If the bubbles persist, recycle the packing (see section A.2).

### A.2 Recycling Sephadex LH-20 Column Packing

**NOTE:** When the column no longer maintains its calibration with azulene/perylene, recycle the packing.

1. Decant any solvent in the column reservoir.
2. Empty the column packing into a beaker 4 times the volume of the packing.
3. Wash with  $\text{CH}_2\text{Cl}_2$ .
4. Add enough  $\text{CH}_2\text{Cl}_2$  to float Sephadex particles in the upper half of the beaker.
5. Remove all glass wool with forceps (mandatory).
6. Cover the beaker and let stand for 1 to 2 hours.
7. Decant the floating particles leaving the sand in the beaker.
8. Aspirate the  $\text{CH}_2\text{Cl}_2$  from the Sephadex particles and set them aside.
9. Swell these particles overnight in 6:4:3 solvent before reusing.

# TOTAL SUSPENDED SOLIDS IN WATERS AND ELUTRIATES

## 1.0 Scope and Application

This method determines the weight of material associated with an aqueous (surface water or elutriate) sample that is suspended and capable of being removed from the sample by filtration.

The filtrate from this procedure may be used in the determination of total dissolved solids.

The end product or residue created from this procedure can be used in the determination of total volatile solids (TVS) in aqueous samples.

Since this method is based on the difference between two weighings, the range and sensitivity of the method is dependent upon the balance used.

The practical range of the determination is 4 mg/L to 20,000 mg/L.

This method is based on EPA Method 160.2 (USEPA, 1983).

## 2.0 Summary of Method

A well-mixed sample is filtered through a glass fiber filter, and the residue retained on the filter is dried to constant weight at 103-105° C.

## 3.0 Interferences

Large floating particles or submerged agglomerates of nonhomogeneous materials should be excluded from the sample if it is determined that their inclusion is not desired in the final result.

For samples high in dissolved solids, thoroughly wash the filter to ensure removal of the dissolved material.

Prolonged filtration times resulting from filter clogging may produce high results owing to excessive solids capture on the clogged filter.

Since the procedure is operationally defined and based on the difference between two weighings, the test is subject to errors due to loss of water of

crystallization, loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics, and decomposition of mineral salts during combustion.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.001 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Convection oven.
4. Thermometer, 0 to 200° C range, graduated to 1° C.
5. Desiccator and desiccant. Desiccants generally used include: anhydrous calcium sulfate, silica gel, or phosphorus pentoxide. Indicating desiccants are preferable since they show when the desiccant needs to be changed or regenerated.
6. Filter support. Filtering apparatus with reservoir and a coarse (40-60 µm) fritted disc as a filter support.

**NOTE:** Many funnel designs are available in glass or porcelain. Some of the most common are Hirsch or Buchner funnels, membrane filter holders and Gooch crucibles. All are available with coarse fritted disc.

7. Planchet, aluminum or stainless steel, or equivalent.

### 4.2 Materials

1. Glass fiber filter discs, without organic binder, such as Millipore AP-40, Reeves Angel 934-AH, Gelman type A/E, or equivalent.

**NOTE:** Because of the physical nature of glass fiber filters, the absolute pore size cannot be controlled or measured. Terms such as "pore size," collection efficiencies and effective retention are used to define this property in glass fiber filters. Values for these parameters vary for the filters listed above.

2. Suction flask. Should be of sufficient capacity for sample size selected.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Preservation of the sample is not practical; analysis should begin as soon as possible. A holding time of 7 days is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C) to minimize microbiological decomposition of solids between sample collection and sample analysis.

All sample containers must be prewashed with detergents. If samples are to be analyzed for other parameters, acids and Type II water washings may also be required. Either glass or plastic containers can be used for the storage of samples to be analyzed for total suspended solids.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The oven should be monitored to ensure that temperature fluctuation does not exceed  $\pm 2^{\circ}$  C.

## 8.0 Procedure

### 8.1 Preparation of Glass-Fiber Filter Disk

1. Place the glass fiber filter on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible with wrinkled surface up.
2. While vacuum is applied, wash the disc with three successive 20 mL volumes of Type II water.
3. Remove all traces of water by continuing to apply vacuum after water has passed through.
4. Remove filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used.
5. Dry in an oven at 103-105° C for one hour.

**NOTE:** If total volatile solids are to be measured, ignite at 550 ± 10° C for 15 minutes in a muffle furnace.

**NOTE:** Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg).

6. Remove to desiccator and store until needed.
7. Weigh immediately before use.

**NOTE:** After weighing, handle the filter or crucible/filter with forceps or tongs only.

### 8.2 Selection of Filter and Sample Sizes

1. For a 4.7 cm diameter filter, filter 100 mL of sample.

**NOTE:** If weight of captured residue is less than 1.0 mg, the sample volume must be increased to provide at least 1.0 mg of residue.

**NOTE:** If other filter diameters are used, start with a sample volume equal to 7 mL/cm<sup>2</sup> of filter area and collect at least a weight of residue proportional to the 1.0 mg stated above.

**NOTE:** If during filtration of this initial volume the filtration rate drops rapidly, or if filtration time exceeds 5 to 10 minutes, the following scheme is recommended:

- a. Use an unweighed glass fiber filter of choice affixed in the filter assembly.
- b. Add a known volume of sample to the filter funnel and record the time elapsed after selected volumes have passed through the filter. Twenty-five mL increments for timing are suggested.
- c. Continue to record the time and volume increments until filtration rate drops rapidly.
- d. Add additional sample if the filter funnel volume is inadequate to reach a reduced rate.
- e. Plot the observed time versus volume filtered.
- f. Select the proper filtration volume as that just short of the time a significant change in filtration rate occurred.

### 8.3 Sample Analysis

1. Assemble the filtering apparatus and begin suction.
2. Wet the filter with a small volume of Type II water to seat it against the fritted support.
3. Shake the sample vigorously and quantitatively transfer the sample volume selected in 8.2 to the filter using a graduated cylinder.
4. Remove all traces of water by continuing to apply vacuum after sample has passed through.
5. With suction on, wash the graduated cylinder, filter, suspended solids, and filter funnel wall with three portions of Type II water allowing complete drainage between washing.

**NOTE :** Total volume of wash water used should equal approximately 2 mL per cm<sup>2</sup>. For a 4.7 cm filter. the total volume is 30 mL.

6. Remove all traces of water by continuing to apply vacuum after water has passed through.
7. Carefully remove the filter from the filter support. Alternatively, remove crucible and filter from crucible adapter if a Gooch crucible is used.

8. Dry at least one hour at 103-105° C.
9. Cool in a desiccator and weigh.
10. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg or less than 4% of the previous weight, whichever is less).

## 9.0 Quality Control

### 9.1 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 10 percent or less.

### 9.2 Blanks

A minimum of one blank per sample batch should be analyzed. A blank for total suspended solids consists of a filter disk. The weight change of the blank should not be greater than  $\pm 0.5$  mg.

## 10.0 Method Performance

The standard deviation was 5.2 mg/L (coefficient of variation = 33%) at 15 mg/L, 24 mg/L at 242 mg/L, and 13 mg/L at 1707 mg/L in studies by two analysts of four sets of 10 determinations each.

Single laboratory duplicate analyses of 50 samples of water and wastewater were made with a standard deviation of differences of 2.8 mg/L.

## 11.0 Calculations and Reporting

Use the results from the individual weighings to calculate the total suspended solid content of the sample as follows:

$$\text{Total Suspended Solids, mg/L} = \frac{(A - B) \times 1000}{V}$$

where:

A = weight of filter plus dried residue, mg.

B = weight of filter, mg.

V = sample volume, mL.

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. 17th Edition, APHA, New York, New York. p. 2-71 - 2-79.

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. Environmental Protection Agency. 1983. "Methods for the Chemical Analysis of Water and Wastes". EPA-600/4-79-020. U.S. Environmental Protection Agency Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. March.

# TOTAL DISSOLVED SOLIDS IN WATERS AND ELUTRIATES

## 1.0 Scope and Application

This method determines the weight of material associated with an aqueous (surface water or elutriate) sample that is dissolved and is carried through a glass fiber filter into the filtrate.

The filtrate from the total suspended solids procedure may be used in the determination of total dissolved solids in aqueous samples.

The end product or residue created from this procedure can be used in the determination of total volatile solids (TVS) in aqueous samples.

Since this method is based on the difference between two weighings, the range and sensitivity of the method is dependent upon the balance used.

The practical range of the determination is 10 mg/L to 20,000 mg/L.

This method is based on EPA Method 160.1 (USEPA, 1983).

## 2.0 Summary of Method

A well-mixed sample is filtered through a glass fiber filter. The filtrate is evaporated to dryness in a weighed dish and dried to a constant weight at 180° C. The increase in dish weight represents the total dissolved solids.

## 3.0 Interferences

Highly mineralized waters with considerable calcium, magnesium, chloride, and/or sulfate content may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing.

Samples high in bicarbonate require careful and possibly prolonged drying to 180° C to insure complete conversion of bicarbonate to carbonate.

Excessive residue in the dish may form a water-trapping crust, therefore, sample size should be limited to no more than 200 mg of residue.

Since the procedure is operationally defined and based on the difference between two weighings, the test is subject to errors due to loss of water of crystallization, loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics, and decomposition of mineral salts during combustion.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.001 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Convection oven, capable of maintaining  $180 \pm 2^\circ \text{C}$ .
4. Thermometer, 0 to  $200^\circ \text{C}$  range, graduated to  $1^\circ \text{C}$ .
5. Desiccator and desiccant. Desiccants generally used include: anhydrous calcium sulfate, silica gel, or phosphorus pentoxide. Indicating desiccants are preferable since they show when the desiccant needs to be changed or regenerated.
6. Filter support. Filtering apparatus with reservoir and a coarse (40-60  $\mu\text{m}$ ) fritted disc as a filter support.

**NOTE:** Many funnel designs are available in glass or porcelain. Some of the most common are Hirsch or Buchner funnels, membrane filter holders and Gooch crucibles. All are available with coarse fritted disc.

7. Steam bath.

### 4.2 Materials

1. Evaporating dishes, porcelain, 90 mm, 100 mL capacity. (aluminum, Vycor, or platinum weighing dishes may be substituted and smaller size dishes may be used, if required.)
2. Glass fiber filter discs, without organic binder, such as Millipore AP-40, Reeves Angel 934-AH, Gelman type A/E, or equivalent.

**NOTE:** Because of the physical nature of glass fiber filters, the absolute pore size cannot be controlled or measured. Terms such as "pore size," collection efficiencies and effective retention

are used to define this property in glass fiber filters. Values for these parameters vary for the filters listed above.

3. Suction flask. Should be of sufficient capacity for sample size selected.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Preservation of the sample is not practical; analysis should begin as soon as possible. A holding time of 7 days is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C) to minimize microbiological decomposition of solids between sample collection and sample analysis.

All sample containers must be prewashed with detergents. If samples are to be analyzed for other parameters, acids and Type II water washings may also be required. Either glass or plastic containers can be used for the storage of samples to be analyzed for total dissolved solids.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The oven should be monitored to ensure that temperature fluctuation does not exceed  $\pm 2^\circ \text{C}$ .

## 8.0 Procedure

### 8.1 Preparation of Glass-Fiber Filter Disk

1. Place the glass fiber filter on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible with wrinkled surface up.
2. While vacuum is applied, wash the disc with three successive 20 mL volumes of Type II water.
3. Remove all traces of water by continuing to apply vacuum after water has passed through.
4. Discard washings.

### 8.2 Preparation of Evaporating Dish

1. If total volatile solids are to be determined on the sample, the evaporating dish should be heated at  $550 \pm 10^{\circ} \text{C}$  for one hour in a muffle furnace prior to use. Cool and store in desiccator until ready for use.
2. If only total dissolved solids are to be measured, heat the clean evaporating dish to  $180 \pm 2^{\circ} \text{C}$  for one hour. Cool and store in desiccator until ready for use.
3. Weigh evaporating dish immediately before use.

### 8.3 Selection of Filter and Sample Sizes

1. Choose sample volume to yield between 2.5 and 200 mg of dried residue.
2. If more than 10 minutes are required to complete filtration, increase filter size or decrease sample volume but do not produce less than 2.5 mg of residue.

### 8.4 Sample Analysis

1. Assemble the filtering apparatus and begin suction.
2. Wet the filter with a small volume of Type II water to seat it against the fritted support.
3. Shake the sample vigorously and quantitatively transfer the well-mixed sample volume to the filter.

4. Wash with three 10 mL portions of Type II water allowing complete drainage between washing.
5. Continue suction for about 3 minutes after filtration is complete.
6. Transfer filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath.

**NOTE:** If filtrate volume exceeds dish capacity, add successive portions to the same dish after evaporation.

7. Dry at least one hour at  $180 \pm 2^\circ \text{C}$ .
8. Cool in a desiccator to balance temperature and weigh.
9. Repeat the drying cycle (steps 7 and 8) until a constant weight is obtained (weight loss is less than 0.5 mg or less than 4% of the previous weight, whichever is less).

## 9.0 Quality Control

### 9.1 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 10 percent or less.

### 9.2 Blanks

A minimum of one blank per sample batch should be analyzed. A blank for total dissolved solids consists of a clean evaporating dish. The weight change of the blank should not be greater than  $\pm 0.5 \text{ mg}$ .

## 10.0 Method Performance

Single laboratory analyses of 77 samples of a known of 293 mg/L were made with a standard deviation of differences of 21.20 mg/L.

## 11.0 Calculations and Reporting

Use the results from the individual weighings to calculate the total dissolved solid content of the sample as follows:

$$\text{Total Dissolved Solids, mg/L} = \frac{(A - B) \times 1000}{V}$$

where:

A = weight of dish plus dried residue, mg.

B = weight of dish, mg.

V = sample volume, mL.

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. 17th Edition, APHA, New York, New York. p. 2-71 - 2-79.

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. Environmental Protection Agency. 1983. "Methods for the Chemical Analysis of Water and Wastes". EPA-600/4-79-020. U.S. Environmental Protection Agency Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. March.

# TOTAL VOLATILE SOLIDS IN WATERS AND ELUTRIATES

## 1.0 Scope and Application

This method determines the weight of material associated with an aqueous (surface water or elutriate) sample that is volatile or combustible at 550° C. The test is useful in obtaining a rough approximation of the amount of organic matter present in the solid fraction of waters or elutriates.

The solid materials used for the determination of total volatile solids may be obtained from the residue obtained in the determination of total dissolved or total suspended solids or from the original sample.

**NOTE:** If the aliquot is obtained from the original sample, then the procedure for total suspended or total dissolved solids must be performed on the aliquot prior to ashing in the muffle furnace.

Since this method is based on the difference between two weighings, the range and sensitivity of the method is dependent upon the balance used.

This method is based on EPA Method 160.4 (USEPA, 1983).

## 2.0 Summary of Method

The residue obtained from the determination of total suspended or total dissolved solids is ignited at 550° C in a muffle furnace. The loss of weight on ignition is reported as mg/L volatile residue.

## 3.0 Interferences

Since the procedure is operationally defined and based on the difference between two weighings, the test is subject to errors due to loss of water of crystallization, loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics, and decomposition of mineral salts during combustion.

The principal source of error in the determination is failure to obtain a representative sample.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.001 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Muffle furnace.
4. Thermocouple, 0 to 600° C range, graduated to 1° C.
5. Desiccator and desiccant. Desiccants generally used include: anhydrous calcium sulfate, silica gel, or phosphorus pentoxide. Indicating desiccants are preferable since they show when the desiccant needs to be changed or regenerated.

### 4.2 Materials

1. Evaporating dishes or crucibles, porcelain, 90 mm, 100 mL capacity. (Aluminum, Vycor, or platinum weighing dishes or crucibles may be substituted and smaller size dishes may be used, if required.)

## 5.0 Reagents and Standards

No reagents are required for this procedure.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Preservation of the sample is not practical; analysis should begin as soon as possible. A holding time of 7 days is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C) to minimize microbiological decomposition of solids between sample collection and sample analysis.

All sample containers must be prewashed with detergents. If samples are to be analyzed for other parameters, acids and Type II water washings may also be required. Either glass or plastic containers can be used for the storage of samples to be analyzed for total volatile solids.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The oven should be monitored to ensure that temperature fluctuation does not exceed  $\pm 2^{\circ}$  C.

## 8.0 Procedure

1. Heat muffle furnace to  $550 \pm 10^{\circ}$  C.
2. Ignite residue produced from the determination of either total dissolved or total suspended solids at  $550 \pm 10^{\circ}$  C for one hour in a muffle furnace.
3. Remove the sample dish from the furnace and allow to partially cool until most of the heat has been dissipated (about 15 minutes).
4. Transfer the sample to a desiccator for final cooling.
5. Weigh sample dish to the nearest mg and record final weight of the sample + dish.

## 9.0 Quality Control

### 9.1 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 10 percent or less.

### 9.2 Blanks

A minimum of one blank per sample batch should be analyzed. A blank for total volatile solids consists of an empty dish. The weight change of the blank should not be greater than  $\pm 0.5$  mg.

## 10.0 Method Performance

A collaborative study involving three laboratories examining four samples by means of ten replicates produced a standard deviation of  $\pm 11$  mg/L at a volatile residue concentration of 170 mg/L (APHA, 1989; USEPA, 1983).

## 11.0 Calculations and Reporting

Use the results from the individual weighings to calculate the total volatile solid content of the sample as follows:

$$\text{Total Volatile Solids, mg/L} = \frac{(A - B) \times 100}{V}$$

where:

A = weight of residue plus dish before ignition, mg.

B = weight of the ashed sample plus dish, mg.

V = sample volume, mL.

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. 17th Edition, APHA, New York, New York. p. 2-71 - 2-79.

U.S. Environmental Protection Agency. 1983. "Methods for the Chemical Analysis of Water and Wastes". EPA-600/4-79-020. U.S. Environmental Protection Agency Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. March.

# ELUTRIATE PREPARATION FROM SEDIMENTS

## 1.0 Scope and Application

This method is applicable to the preparation of elutriates from sediment and dredging site water samples. The elutriate test is a simplified simulation of the dredging and disposal process wherein predetermined amounts of dredging site water and sediment are mixed together to approximate a dredged material slurry.

This method is based on the elutriate preparation procedures presented by Plumb (1981).

## 2.0 Summary of Method

Water and sediment samples collected at the dredging site are collected and mixed in a ratio of 1:4 sediment:water. The mixture is shaken vigorously for 30 minutes and allowed to settle undisturbed for 1 hour. The liquid phase is then centrifuged and filtered through a 45  $\mu\text{m}$  membrane filter to remove all suspended particulate matter. The filtrate is the elutriate to be used for testing purposes.

## 3.0 Interferences

Non-representative particulates such as leaves, sticks, fish and lumps of fecal matter should be excluded from the sediment sample if it is determined that their inclusion is not desired in the final result.

Excessive quantities of suspended fine particulates may clog the membrane filter. Additional high speed centrifugation can be used to alleviate this interference.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Centrifuge, capable of handling six 1 or 0.5 L centrifuge bottles at 3000 to 5000 rpm.

2. Laboratory shaker capable of shaking 2 L flasks at approximately 100 excursions/minute. Box type or wrist action shakers are acceptable.
3. Vacuum or pressure filtration equipment including:
  - a. vacuum pump or compressed air source
  - b. appropriate filter holder capable of handling 47, 105, or 155 mm diameter filters

## 4.2 Materials

1. Erlenmeyer flasks, graduated, 1 L, or equivalent.
2. Graduated cylinders, 1 L.
3. Large powder funnels, 15 cm.
4. Membrane filters, 0.45  $\mu\text{m}$  pore size.
5. Volumetric flasks, class A, 1 L.

## 5.0 Reagents and Standards

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
3. Hydrochloric acid, 5 M. Add 417 mL concentrated HCl to 500 mL Type II water. Dilute to 1 liter with Type II water.

## 6.0 Sample Collection, Handling, and Preservation

Sample collection procedures for the waters and sediments should be described in the approved sampling manual. Further information on bulk water and sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

For this procedure, approximately 3 liters of sediment should be collected to provide sufficient elutriates for all parameters and to cover most reanalyses that may be needed/requested.

For this procedure, approximately 12 liters of water should be collected from the dredging site.

**NOTE:** If fill material disposal activity is to be assessed, 12 liters of water should be collected from the disposal site.

No preservation techniques (other than refrigeration - see below) should be applied to the water or sediments to be used in the preparation of elutriates. Analysis should begin as soon as possible after sample collection. A holding time of 7 days is generally cited for the site waters used in the elutriate preparation procedure.

For the elutriate, required preservation techniques for the various parameters are presented in Section 6.0 of each individual method.

Elutriate, sediment, and water samples should be stored under refrigerated conditions (4° C).

**NOTE:** Water and sediment samples should not be frozen or dried prior to use.

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of samples used in the elutriate preparation procedure.

**NOTE:** If trace organic analyses are to be performed, glass containers with Teflon-lined lids are required.

## 7.0 Calibration and Standardization

No calibration or standardization procedures are required during elutriate preparation.

## 8.0 Procedure

1. Place 100 mL of unfiltered dredging site water into a 1 L Erlenmeyer flask.
2. Add homogenized, field-moist sediment via a powder funnel to obtain a total volume of 300 mL.
3. Fill the flask to the 1 L mark with unfiltered dredging site water.

**NOTE:** This procedure should provide 700 - 800 mL of elutriate for analysis.

4. Cap the flask tightly with a noncontaminating stopper and shake vigorously on an automatic shaker at about 100 excursions/minute.

**NOTE:** A polyfilm-covered rubber stopper is generally acceptable for minimum contamination.

**NOTE:** During the mixing step, the oxygen demand of the dredged material may cause the dissolved oxygen concentration to drop to zero. This change can alter the release of chemical contaminants from dredged material to the disposal site water and reduce the reproducibility of the elutriate test. If it is known that anoxic conditions will not occur at the disposal site or if reproducibility of the elutriate test is a potential problem, the mixing may be accompanied by compressed air-mixing instead of by mechanical mixing using the following procedure:

- a. After preparation of the slurry mixture, an air-diffuser tube is inserted almost to the bottom of the flask.
  - b. Compressed air is passed through a Type II water trap and then through the diffuser tube and slurry.
  - c. The air flow rate should be adjusted to agitate the mixture vigorously for 30 minutes.
  - d. Flasks should be manually stirred at 10 minute intervals to ensure complete mixing.
5. After 30 minutes of shaking or mixing with air, allow the suspension to settle undisturbed for 1 hour.
  6. Carefully decant the supernatant into appropriate centrifuge bottles.
  7. Select a time and centrifuge speed that will substantially reduce the suspended solids concentration.

**NOTE:** The time and speed will be vary depending upon the particle-size distribution of the sediment. More clayey sediment may require longer times at higher speeds than sandy sediments.

8. Filter approximately 100 mL of sample through a 45  $\mu\text{m}$  membrane filter and discard the filtrate.

**NOTE:** The filters should be soaked in 5 M HCl for at least 2 hours prior to use.

9. Filter the remainder of the sample to give a clear elutriate.

**NOTE:** Store the elutriate at 4° C.

**NOTE:** Analyze the elutriate as soon as possible after extraction using the methods specified in this appendix. If necessary, addition of the preservatives specified for the parameters in their respective analytical methods may be added to a subsample of the elutriate sample.

## 9.0 Quality Control

No quality control procedures are required for elutriate preparation. If precision within a given bulk sediment sample (i.e., a very heterogenous sediment) is a concern, multiple elutriate samples can be prepared and analyzed as separate routine samples.

**NOTE:** Analytical replicates are required within each of the analytical procedures within this appendix.

## 10.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

Plumb, R.H., Jr. 1981. Procedure for Handling and Chemical Analysis of Sediment and Water Samples. Tech. Rep. EPA/CE-81-1. U.S. Army Engineer Waterways Expt. Station, Vicksburg, MS.

# AMMONIA NITROGEN IN WATERS AND ELUTRIATES (COLORIMETRIC, AUTOMATED)

## 1.0 Scope and Application

This method covers the determination of ammonia in surface water and sediment elutriates in the range of 0.01 to 2.0 mg/L NH<sub>3</sub> as N. This range is for photometric measurements made at 630-660 nm in a 15 mm or 50 mm tubular flow cell. Higher concentrations can be determined by sample dilution. Approximately 20 to 60 samples per hour can be analyzed.

This procedure is based on Method 350.1 (APHA, 1989).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside. The intensity of the color is automatically determined by measuring sample absorbance at 630 nm.

## 3.0 Interferences

Calcium and magnesium ions may be present in concentration sufficient to cause precipitation problems that may interfere with the colorimetric analysis. A 5% EDTA solution is used to prevent the precipitation of calcium and magnesium ions when fresh water samples are analyzed.

Sample turbidity and color may interfere with this method. Turbidity must be removed by filtration prior to analysis. Sample color that absorbs in the photometric range used will also interfere. It may be necessary to distill ammonia from high-color content samples prior to analysis.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Technicon AutoAnalyzer Unit (AAI or AAI) consisting of:
  - a. sampler,
  - b. manifold (AAI) or analytical cartridge (AAI),
  - c. proportioning pump,
  - d. heating bath with double delay coil (AAI),
  - e. colorimeter equipped with 15 mm tubular flow cell and 630-660 nm filters,
  - f. recorder, and
  - g. digital printer for AAI (optional).

### 4.2 Materials

1. Volumetric flask, class A, 100 mL.
2. Volumetric flask, class A, 1 L.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.

**NOTE:** Type II water: Special precaution must be taken to insure that this Type II water is free of ammonia. Such water is prepared by passage of Type II water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. The regeneration of the ion exchange column should be carried out according to the instruction of the manufacturer. All solutions must be made using ammonia-free Type II water.

2. Disodium ethylenediamine-tetraacetate (EDTA), 5%. Dissolve 50 g of EDTA (disodium salt) and approximately six pellets of NaOH in 1 liter of Type II water.

3. Sodium hypochlorite (NaOCl) solution. Dilute 250 mL of a bleach solution containing 5.25% NaOCl (such as "Clorox") to 500 mL with Type II water. Available chlorine level should approximately 2 to 3%.

**NOTE:** Since "Clorox" is a proprietary product, its formulation is subject to change. The analyst must remain alert to detecting any variation in this product significant to its use in this procedure. Due to the instability of this product, storage over an extended period should be avoided.

4. Sodium nitroprusside ( $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot\text{H}_2\text{O}$ ), 0.05%. Dissolve 0.5 g of sodium nitroprusside in 1 liter of Type II water.
5. Sodium phenolate. Using a 1 liter Erlenmeyer flask, dissolve 83 g phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) in 500 mL of Type II water. In small increments, cautiously add with agitation, 32 g of NaOH. Periodically cool flask under water faucet. When cool, dilute to 1 liter with Type II water.
6. Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ), reagent grade. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
7. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), 5 N, for use as the air scrubber solution. Carefully add 139 mL of concentrated sulfuric acid to approximately 500 mL of ammonia-free Type II water. Cool to room temperature and dilute to 1 liter with ammonia-free Type II water.
8. Ammonia stock solution. Dissolve 3.819 g of anhydrous ammonium chloride ( $\text{NH}_4\text{Cl}$ ), dried at  $105^\circ\text{C}$ , in Type II water. Dilute to 1 liter with Type II water. (1.0 mg/mL  $\text{NH}_3\text{-N}$ ).
9. Standard solution A. Dilute 10.0 mL of ammonia stock solution to 1 liter with Type II water. (0.01 mg/mL  $\text{NH}_3\text{-N}$ ).
10. Standard solution B. Dilute 10.0 mL of standard solution A to 1 liter with Type II water. (0.001 mg/mL  $\text{NH}_3\text{-N}$ ).

## 6.0 Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Aqueous samples should be preserved by adding 2 mL concentrated H<sub>2</sub>SO<sub>4</sub> per liter. The final pH of acid-preserved samples should be between 1.5 and 2.0. When samples are preserved in this manner, a pH adjustment of the samples and/or the analytical standards may be required before analysis is completed.

A holding time of 28 days after sample collection is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of aqueous samples to be analyzed for ammonia.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Using standard solutions A and B, prepare the following standards in 100 mL volumetric flasks (prepare fresh daily):

<u>NH<sub>3</sub>-N, mg/L</u>	<u>mL Standard Solution/100 mL</u>
	<u>Solution B</u>
0.01	1.0
0.02	2.0
0.05	5.0
0.10	10.0
	<u>Solution A</u>
0.20	2.0
0.50	5.0
0.80	8.0
1.00	10.0
1.50	15.0
2.00	20.0

## 8.0 Procedure

The intensity of the color developed between ammonia and the colorimetric reagents is pH dependent. In order to compensate for this effect, the pH of the samples, the standard ammonia solutions, and the wash water should be similar. This can be accomplished by either (1) adding 2 mL concentrated H<sub>2</sub>SO<sub>4</sub> per liter to the standards and wash water or (2) neutralizing the pH of the samples with NaOH or KOH.

1. Select the appropriate manifold for the automated analyses to be run. For a working range of 0.01 to 2.00 mg NH<sub>3</sub>-N/L use the AAI set up. For a working range of .01 to 1.0 mg NH<sub>3</sub>-N/L, use the AAll set up. Higher concentrations may be accommodated by sample dilution.

**NOTE:** Manifold flow rates for the AAI set up are as follows:

Wash Water	2.0 mL/min.
Sample	0.42 mL/min.
EDTA	0.8 mL/min.
Air*	0.23 mL/min.
Na-phenolate	0.42 mL/min.
Na-hypochlorite	0.32 mL/min.
Na-nitroprusside	0.42 mL/min.

**NOTE:** Manifold flow rates for the AAll set up are as follows:

Wash Water	2.9 mL/min.
Sample	2.0 mL/min.
EDTA	0.8 mL/min.
Air*	2.0 mL/min.
Na-phenolate	0.6 mL/min.
Na-hypochlorite	0.6 mL/min.
Na-nitroprusside	0.6 mL/min.

\* = air should be scrubbed through 5 N H<sub>2</sub>SO<sub>4</sub>

2. Allow both colorimeter and recorder to warm up for 30 minutes.
3. Obtain a stable baseline with all reagents, feeding Type II water through sample line.

4. For the AAI system, sample at a rate of 20/hr. 1:1. For the AAll, use a 60/hr 6:1 cam with a common wash.
5. Arrange ammonia standards in the sampler in order of decreasing ammonia concentration.
6. Complete loading of the sampler tray with routine and quality assurance/quality control samples.
7. Switch sample line from distilled water to sampler and begin analysis.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for ammonia in aqueous solutions is 30 µg/L.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured ammonia concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 10.0 Method Performance

In a single laboratory (EMSL-CIN), using surface water samples at concentrations of 1.41, 0.77, 0.59 and 0.43 mg NH<sub>3</sub>-N/L, the standard deviation was  $\pm 0.005$ . In a second single laboratory study (Alberta Pollution Control Laboratory), the calculated coefficient of variation for surface water samples with ammonia concentrations of 0.029, 0.060, and 0.093 mg/L NH<sub>3</sub>-N were 4.7, 2.0, and 1.1%, respectively.

In a single laboratory (EMSL-CIN), using surface water samples at concentrations of 0.16 and 1.44 mg NH<sub>3</sub>-N/L, recoveries were 107 and 99%, respectively. In a second single laboratory study (Alberta Pollution Control Laboratory), using surface water samples with NH<sub>3</sub>-N concentrations of 0.008, 0.015, and 0.039 mg/L, the recoveries were 104, 97, and 105%, respectively.

## 11.0 Calculations and Reporting

The resultant ammonia concentrations can be obtained by comparison of sample peak heights to the standard curve of peak heights of the standards plotted against their corresponding known concentration values.

## 12.0 References

Alberta Environmental Centre. 1981. Methods Manual for Chemical Analysis of Water and Wastes. Environment Canada, Vegreville, Alberta, Canada.

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. Method 4500-NH<sub>3</sub> H. 17th Edition, APHA, New York, New York. p. 4-126.

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

Booth, R. L., and L.B. Lobring. 1973. Evaluation of the AutoAnalyzer II: A Progress Report". In Advances in Automated Analysis 8:7-10. 1972 Technicon International Congress. Mediad Incorporated, Tarrytown, N.Y.

Fiore, J., and J.E. O'Brien. 1962. Ammonia Determination by Automatic Analysis. Wastes Engineering 33:352.

Hiller, A., and D. Van Slyke. 1933. Determination of Ammonia in Blood. J. Biol. Chem. 102:499.

O'Connor, B., R. Dobbs, B. Villiers, and R. Dean. 1967. Laboratory Distillation of Municipal Waste Effluents. JWPCF 39:25.

# AMMONIA NITROGEN IN WATERS AND ELUTRIATES (COLORIMETRIC, MANUAL)

## 1.0 Scope and Application

This method covers the determination of ammonia in surface water and sediment elutriates in the range of 0.05 to 1.0 mg NH<sub>3</sub>-N/L for the colorimetric procedure. The measurements are made colorimetrically at 425 nm. Higher concentrations can be determined by sample dilution.

This procedure is based on Method 350.2 (APHA, 1989).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia in the distillate is determined colorimetrically by nesslerization.

## 3.0 Interferences

A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity upon the addition of Nessler reagent, so direct nesslerization (i.e., without distillation), has been discarded as an official method.

Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out. Volatile alkaline compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization in the distillation method. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH (approximately 2 to 3) prior to distillation and nesslerization.

Residual chlorine must also be removed by pretreatment of the sample with sodium thiosulfate or sodium arsenite before distillation.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Kjeldahl distillation apparatus.
4. Spectrophotometer or filter photometer for use at 425 nm and providing a light path of 1 cm or more.

### 4.2 Materials

1. Erlenmeyer flask, 500 mL. These flasks should be marked at the 350 and the 500 mL volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.
2. Kjeldahl flask, 800 mL.
3. Nessler tubes. Matched Nessler tubes (APHA Standard) about 300 mm long, 17 mm inside diameter, and marked at 225 mm  $\pm$  1.5 mm inside measurement from bottom.
4. Volumetric flask, class A, 100 mL.
5. Volumetric flask, class A, 1 L.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.

**NOTE:** Special precaution must be taken to insure that this Type II water is free of ammonia. Such water is prepared by passage of Type II water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. The regeneration of the ion exchange column should be carried out according to the instruction of the manufacturer. All solutions must be made using ammonia-free Type II water.

2. Borate buffer. Add 88 mL of 0.1 N NaOH solution to 500 mL of 0.025 M sodium tetraborate solution (5.0 g anhydrous  $\text{Na}_2\text{B}_4\text{O}_7$  or 9.5 g  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  per liter). Dilute to 1 liter with Type II water.

3. Boric acid solution, 2%. Dissolve 20 g  $\text{H}_3\text{BO}_3$  in ammonia-free Type II water. Dilute to 1 liter with Type II water.
4. Dechlorinating reagents. A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:
  - a. Sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ), 0.014 N. Dissolve 3.5 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in ammonia-free Type II water. Dilute to 1 liter with Type II water.

**NOTE:** One mL of this solution will remove 1 mg/L of residual chlorine in 500 mL of sample.

- b. Sodium arsenite ( $\text{NaAsO}_2$ ), 0.014 N. Dissolve 1.0 g  $\text{NaAsO}_2$  in ammonia-free Type II water. Dilute to 1 liter with Type II water.
6. Nessler reagent. Dissolve 100 g of mercuric iodide (Hgl) and 70 g of potassium iodide (KI) in a small amount of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 mL of Type II water. Dilute to 1 liter with Type II water.

**NOTE:** If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.

**NOTE:** This reagent should give the characteristic color with ammonia within 10 minutes after addition and should not produce a precipitate with small amounts of ammonia ( $\leq 0.04$  mg/50 mL).

7. Sodium hydroxide (NaOH), 1 N: Dissolve 40 g NaOH in ammonia-free Type II water. Dilute to 1 liter with Type II water.
8. Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ), reagent grade. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration  $< \text{MDL}$ , then the acid can be used.
9. Sulfuric acid stock solution, 0.1 N. Add 3 mL of concentrated  $\text{H}_2\text{SO}_4$  to 1 liter of  $\text{CO}_2$ -free Type II water.
10. Sulfuric acid standard solution, 0.02 N (0.28 mg/mL  $\text{NH}_3\text{-N}$ ). Dilute 200 mL of the sulfuric acid stock solution to 1 liter with  $\text{CO}_2$ -free Type II water.
11. Ammonia stock solution. Dissolve 3.819 g of anhydrous ammonium chloride ( $\text{NH}_4\text{Cl}$ ), dried at  $105^\circ \text{C}$ , in Type II water. Dilute to 1 liter with Type II water. (1.0 mg/mL  $\text{NH}_3\text{-N}$ ).

12. Ammonia standard solution. Dilute 10.0 mL of ammonia stock solution to 1 liter with Type II water. (0.01 mg/mL NH<sub>3</sub>-N).

## 6.0 Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Aqueous samples should be preserved by adding 2 mL concentrated H<sub>2</sub>SO<sub>4</sub> per liter. The final pH of acid-preserved samples should be between 1.5 and 2.0. When samples are preserved in this manner, a pH adjustment of the samples and/or the analytical standards may be required before analysis is completed.

A holding time of 28 days after sample collection is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of aqueous samples to be analyzed for ammonia.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Prepare a series of Nessler tube standards as follows:

<u>mL of Standard</u> <u>(0.01 mg/mL NH<sub>3</sub>-N)</u>	<u>mg NH<sub>3</sub>-N/50.0 mL</u>
0.0	0.0
0.5	0.005
1.0	0.01
2.0	0.02
3.0	0.03
4.0	0.04
5.0	0.05
8.0	0.08
10.0	0.10

Dilute each tube to 50 mL with Type II water. Add 2.0 mL of Nessler reagent. Mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained, plot absorbance vs. mg NH<sub>3</sub>-N for the standard curve.

The sulfuric acid standard solution must be standardized following one of the two following methods:

- Standardize the approximately 0.02 N acid against 0.0200 N Na<sub>2</sub>CO<sub>3</sub> solution. This sodium carbonate solution is prepared by dissolving 1.060 g anhydrous Na<sub>2</sub>CO<sub>3</sub>, oven-dried at 140° C, and diluting to 1 liter with CO<sub>2</sub>-free Type II water.
- Standardize the approximately 0.1 N H<sub>2</sub>SO<sub>4</sub> solution against a 0.100 N Na<sub>2</sub>CO<sub>3</sub> solution. By proper dilution, the 0.02 N acid can then be prepared.

The later method (b.) is preferable.

## 8.0 Procedure

### 8.1 Preparation of Equipment

- Add 500 mL of Type II water to an 800 mL Kjeldahl flask.

**NOTE:** The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping.

2. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.

## 8.2 Sample Preparation

1. Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual.
2. Add 1 N NaOH to 400 mL of sample, until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.

## 8.3 Sample Distillation

1. Transfer the sample, the pH of which has been adjusted to 9.5, to a 800 mL Kjeldahl flask.
2. Add 25 ml of the borate buffer.
3. Distill 300 mL at the rate of 610 mL/min. into 50 mL of 2% boric acid contained in a 500 mL Erlenmeyer flask.

**NOTE:** The condenser tip or an extension of the condenser tip must extend below the level of the boric acid solution.

4. Dilute the distillate to 500 mL with Type II water.

## 8.4 Colorimetric Analysis

1. Allow the spectrophotometer to warm up for 30 minutes.
2. Add 2.0 mL of Nessler reagent to 50 mL of the distillate in a Nessler tube. Mix.
3. After 20 minutes, read the absorbance at 425 nm.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for ammonia in aqueous solutions is 30 µg/L.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured ammonia concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

### 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 10.0 Method Performance

Twenty-four analysts in sixteen laboratories analyzed natural water samples containing exact increments of an ammonium salt with the following results:

<u>Increment as</u>		<u>Precision as</u>	<u>Accuracy as</u>
Nitrogen, Ammonia		Standard Deviation	Bias
mg N/L	mg N/L	%	mg N/L
0.21	0.122	-5.54	-0.01
0.26	0.070	-18.12	-0.05
1.71	0.244	+0.46	+0.01
1.92	0.279	-2.01	-0.04

## 11.0 Calculations and Reporting

The initial ammonia concentrations can be obtained by comparison of sample peak heights to the standard curve of peak heights of the standards plotted against their corresponding known concentration values. These values are then adjusted for dilution effects using the following formula:

$$\text{NH}_3\text{-N, mg/L} = \frac{A \times B \times 1,000}{D \times C}$$

where:

A = NH<sub>3</sub>-N read from standard curve, mg.

B = total distillate collected including boric acid and any dilution, mL.

C = distillate taken for nesslerization, mL.

D = volume of original sample taken, mL.

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. Method 4500-NH<sub>3</sub> H. 17th Edition, APHA, New York, New York. p. 4-126.

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

# CYANIDE IN WATERS AND ELUTRIATES (COLORIMETRIC, AUTOMATED UV)

## 1.0 Scope and Application

This method is used to determine the concentration of inorganic cyanide in aqueous samples, such as surface water and elutriate samples. The method detects inorganic cyanides that may be present as either simple soluble salts or complex radicals.

The colorimetric method is sensitive to approximately 0.02 mg/L of cyanide and is recommended for concentrations below 1 mg/L. The range of the procedure can be adjusted by modifying the sample preparation technique or the cell path length. However, the amount of sodium hydroxide in the standards and the sample to be analyzed must be the same.

This procedure is based on SW-846 Method 9012 (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" to waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

A sample aliquot is treated with strong acid to convert any cyanides that may be present to hydrocyanic acid (HCN). This material is isolated from the original sample matrix by a process of distillation and trapped in a sodium hydroxide solution. The resultant cyanide concentration is determined by automated UV colorimetry.

Cyanide in the distillate is reacted with chloramine-T at a pH less than 8 to produce cyanogen chloride (CNCl). After this reaction is complete, the addition of pyridine-barbituric acid reagent produces a red-blue color that is proportional to the cyanide concentration. The intensity of the color is automatically determined by measuring sample absorbance at 570 nm. The concentration of NaOH must be the same in the standards, the sample distillate, and any dilutions of the original sample distillate to obtain colors of comparable intensity.

### 3.0 Interferences

Oxidizing agents such as chlorine will decompose most cyanides. Chlorine interferences can be eliminated by adding an excess of ascorbic acid to the sample prior to preservation and storage (Section 6). This will reduce the chlorine to chloride which does not interfere with the colorimetric procedure.

Sulfides adversely affect the development of color in the analytical procedure. This interference can be reduced or eliminated by adding bismuth nitrate to the samples to precipitate the sulfide prior to distillation (Section 8.1.4). Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce sulfide during the distillation procedure should also be treated with bismuth nitrate prior to distillation.

Nitrate and/or nitrite in samples can act as a positive interference when present at concentrations above 10 mg/L and in the presence of certain organic compounds. These nitrogen compounds can form nitrous acid during the distillation process which will react with some organic compounds to form oxides. These oxides will decompose under conditions developed in the colorimetric procedure to generate HCN. This interference is eliminated by treating the samples with sulfamic acid prior to distillation (Section 8.1.5).

### 4.0 Apparatus and Materials

#### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Reflux distillation apparatus. The boiling flask should be of 1-liter size with inlet tube and provision for condenser. The gas absorber is a Fisher-Milligan scrubber (Fisher Catalog #07-513), or equivalent.
4. Automated continuous-flow analytical instrument with:
  - a. sampler,
  - b. manifold with UV digester,
  - c. proportioning pump,
  - d. heating bath with distillation coil,
  - e. distillation head,

- f. colorimeter equipped with a 15 mm flow cell and 570 nm filter, and
- g. recorder.

## 4.2 Materials

1. Potassium iodide-starch test paper.
2. Volumetric flasks, class A, 250 mL.
3. Volumetric flasks, class A, 100 mL.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Ascorbic acid ( $C_6H_8O_6$ ), analytical reagent grade crystals.
3. Bismuth nitrate solution ( $Bi(NO_3)_3$ ). Dissolve 30.0 grams of  $Bi(NO_3)_3$  in 100 mL of Type II water. While stirring, add 250 mL of glacial acetic acid. Stir until dissolved. Dilute to 1 liter with Type II water.
4. Chloramine-T solution. Dissolve 1.0 g of white, water-soluble, chloramine-T in 100 mL of Type II water. Refrigerate until ready to use.
5. Concentrated acetic acid ( $C_4H_6O_3$ ), glacial, reagent grade. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
6. Concentrated sulfuric acid ( $H_2SO_4$ ), reagent grade. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
7. Sulfuric acid (1:1). Slowly add 500 mL of concentrated  $H_2SO_4$  to 500 mL of Type II water.

**CAUTION:** This is an exothermic reaction.

8. Magnesium chloride solution ( $MgCl_2 \cdot 6H_2O$ ). Dissolve 510 g of  $MgCl_2 \cdot 6H_2O$  into a 1 liter flask. Dilute to 1 liter with Type II water.
9. Pyridine-barbituric acid reagent. Place 15 g of barbituric acid ( $C_4H_4O_3N_2$ ) in a 250 mL volumetric flask. Add just enough Type II water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine ( $C_5H_5N$ ) and mix. Add 15 mL of concentrated HCl. Allow to

cool to room temperature. Dilute to 250 mL with Type II water. This reagent is stable for approximately six months, if stored in a cool, dark place.

10. Sodium dihydrogenphosphate ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ), 1 M. Dissolve 138 g of  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  in 1 liter of Type II water.
11. Sodium hydroxide solution (NaOH), 1.25 N. Dissolve 50 g of NaOH in Type II water. Dilute to 1 liter with Type II water.
12. Sodium hydroxide solution (NaOH), 1 N. Dissolve 40 g of NaOH in Type II water. Dilute to 1 liter with Type II water.
13. Sodium hydroxide dilution water and receptacle wash water (NaOH), 0.25 N. Dissolve 10.0 g NaOH in 500 mL of Type II water. Dilute to 1 liter with Type II water.
14. Sulfamic acid solution ( $\text{NH}_2\text{SO}_3\text{H}$ ). Dissolve 40 g of sulfamic acid in Type II water. Dilute to 1 liter with Type II water.
15. Cyanide stock solution. Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of Type II water. Standardize with 0.0192 N  $\text{AgNO}_3$ . Dilute to appropriate concentration of 1 mg/mL.
16. Intermediate standard cyanide solution. Dilute 100.0 mL of stock cyanide solution to 1 liter with Type II water (100  $\mu\text{g}/\text{mL}$  CN).
17. Working standard cyanide solution. Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1 liter with Type II water (10.0  $\mu\text{g}/\text{mL}$  CN). Store in a glass-stoppered bottle.

**NOTE:** All working standards should contain 2 mL of 1 N NaOH per 100 mL.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Aqueous samples should be immediately preserved in the field by the addition of 10 N sodium hydroxide until the sample pH is  $\geq 12$ . A holding time of 14 days after sample collection is generally cited for this parameter.

Oxidizing agents, such as chlorine, decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with

acidified potassium iodide (KI)-starch test paper as soon as the sample is collected. A blue color indicates the need for treatment. Add ascorbic acid a few crystals at a time until a drop of sample produces no color on the indicator. Then add an additional 0.6 g of ascorbic acid for each liter of water.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of aqueous samples to be analyzed for cyanide.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Two methods are given for preparing a standard cyanide curve. Section 7.1 should be followed if the samples do not contain sulfide and Section 7.2 should be followed if the samples to be analyzed contain sulfide. The difference between these two methods is that all the cyanide standards must be carried through the sample distillation process when sulfide is present.

### 7.1 Standard Curve for Samples without Sulfide.

1. Prepare a series of standards by pipetting suitable volumes of the working standard cyanide solution into 250 mL volumetric flasks. To each standard add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with Type II water. Prepare as follows:

mL of Working Standard Solution (1 mL = 10 µg CN)	Concentration (µg CN/250 mL)
0.0	BLANK
1.0	10
2.0	20
5.0	50
10.0	100
15.0	150
20.0	200

It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and a low) be distilled and compared with similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within  $\pm 10\%$  of the undistilled standards, the analyst should find the cause of the apparent error before proceeding.

2. Prepare a standard curve by plotting absorbances of standards vs. cyanide concentrations.
3. To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard cyanide solution or the working standard cyanide solution to 500 mL of sample to ensure a level of 20  $\mu\text{g/L}$ . Proceed with the analysis as in Section 8.1 - Sample Distillation.

## 7.2 Standard Curve for Samples with Sulfide

1. All standards must be distilled in the same manner as the samples. A minimum of three standards shall be distilled.
2. Prepare a standard curve by plotting absorbance of standards vs. cyanide concentration.

## 8.0 Procedure

### 8.1 Sample Distillation

1. Place 500 mL of sample, or an aliquot diluted to 500 mL, in a 1 liter boiling flask.
2. Pipet 50 mL of 1.25 N sodium hydroxide solution into the absorbing tube of the reflux distillation apparatus. Connect the boiling flask, condenser, absorber, and trap in the train.
3. Adjust the vacuum source to allow a slow stream of air to enter the boiling flask. Approximately two bubbles of air per second should enter the boiling flask.
4. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper.

**NOTE:** If test is positive, treat the sample by adding 50 mL of bismuth nitrate solution through the air inlet tube after the air rate is set. Mix for 3 minutes prior to addition of  $\text{H}_2\text{SO}_4$  in step 6.

5. If samples are suspected to contain  $\text{NO}_3$  and/or  $\text{NO}_2$ , add 50 mL of sulfamic acid solution after the air rate is set through the air inlet tube. Mix for 3 min prior to addition of  $\text{H}_2\text{SO}_4$ .
6. Slowly add 50 mL 1:1  $\text{H}_2\text{SO}_4$  through the air inlet tube.
7. Rinse the tube with Type II water and allow the airflow to mix the flask contents for 3 min.
8. Pour 20 mL of magnesium chloride into the air inlet and wash down with stream of water.
9. Heat the solution to boiling. Reflux for 1 hr. Turn off heat and continue the airflow for at least 15 min. After cooling the boiling flask, disconnect absorber and close off the vacuum source.
10. Drain the solution from the absorber into a 250 mL volumetric flask. Wash the absorber with Type II water and add the washings to the flask. Dilute to the 250 mL with Type II water. The sample is now ready for analysis.

## 8.2 Automated Colorimetric Determination

1. Set up the manifold in a hood or a well-ventilated area.
2. Allow colorimeter and recorder to warm up for 30 min.
3. Run a baseline with all reagents feeding Type II water through the sample line.
4. Place appropriate standards in the sampler in order of decreasing concentration.
5. Complete loading of the sampler tray with unknown and quality assurance/quality control samples.
6. When the baseline becomes steady, begin the analysis.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for cyanide in aqueous solutions is 5000  $\mu\text{g/L}$ .

## 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured cyanide concentrations.

## 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

## 9.4 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the instrument detection limit.

## 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.6 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - cyanide, to the 100 mL aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The matrix spike should be prepared by adding cyanide from the working standard or intermediate cyanide standard to ensure a final concentration of approximately 40  $\mu\text{g/L}$ . The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration.

Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 20\%$ .

## 10.0 Method Performance

In a single laboratory (EMSL-CIN) test, using mixed industrial and domestic waste samples at concentrations of 0.06, 0.13, 0.28, and 0.62 mg/L CN, the precision standard deviations were  $\pm 0.005$ ,  $\pm 0.007$ ,  $\pm 0.031$ , and  $\pm 0.094$ , respectively.

In the same single laboratory (EMSL-CIN) test, using mixed industrial and domestic waste samples at 0.28 and 0.62 mg/L CN, the analyte recoveries were 85% and 102%, respectively.

## 11.0 Calculations and Reporting

The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences, such as those that contain sulfide (see section 11.1). The results of all other colorimetric analyses can be obtained by comparison of sample peak heights to the standard curve of peak heights of the standards plotted against their corresponding known concentration values.

### 11.1 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. Method 4500-CN C and 4500-CN E. 17th Edition, APHA, New York, New York. p. 4-29 - 4-31.

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

Goulden, P.D., B.K. Afghan, and P. Brooksbank. 1972. Determination of Nanogram Quantities of Simple and Complex Cyanides in Water. Anal. Chem. 44:1845-49.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

# CYANIDE IN WATERS AND ELUTRIATES (COLORIMETRIC, MANUAL)

## 1.0 Scope and Application

This method is used to determine the concentration of inorganic cyanide in aqueous samples, such as surface water and elutriate samples. The method detects inorganic cyanides that may be present as either simple soluble salts or complex radicals.

The colorimetric method is sensitive to approximately 0.02 mg/L of cyanide and is recommended for concentrations below 1 mg/L. The range of the procedure can be adjusted by modifying the sample preparation technique or the cell path length. However, the amount of sodium hydroxide in the standards and the sample to be analyzed must be the same.

This procedure is based on SW-846 Method 9010A (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

A sample aliquot is treated with strong acid to convert any cyanides that may be present to hydrocyanic acid (HCN). This material is isolated from the original sample matrix by a process of distillation and trapped in a sodium hydroxide solution. The resultant cyanide concentration is determined colorimetrically.

Cyanide in the distillate is reacted with chloramine-T at a pH less than 8 to produce cyanogen chloride (CNCl). After this reaction is complete, the addition of pyridine-barbituric acid reagent produces a red-blue color that is proportional to the cyanide concentration. The intensity of the color is measured by measuring sample absorbance at 578 nm. The concentration of NaOH must be the same in the standards, the sample distillate, and any dilutions of the original sample distillate to obtain colors of comparable intensity.

### 3.0 Interferences

Oxidizing agents such as chlorine will decompose most cyanides. Chlorine interferences can be eliminated by adding an excess of ascorbic acid to the sample prior to preservation and storage (Section 6). This will reduce the chlorine to chloride which does not interfere with the colorimetric procedure.

Sulfides adversely affect the development of color in the analytical procedure. This interference can be reduced or eliminated by adding bismuth nitrate to the samples to precipitate the sulfide prior to distillation (Section 8.1.4). Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce sulfide during the distillation procedure should also be treated with bismuth nitrate prior to distillation.

Nitrate and/or nitrite in samples can act as a positive interference when present at concentrations above 10 mg/L and in the presence of certain organic compounds. These nitrogen compounds can form nitrous acid during the distillation process which will react with some organic compounds to form oxides. These oxides will decompose under conditions developed in the colorimetric procedure to generate HCN. This interference is eliminated by treating the samples with sulfamic acid prior to distillation (Section 8.1.5).

### 4.0 Apparatus and Materials

#### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Reflux distillation apparatus. The boiling flask should be of 1-liter size with inlet tube and provision for condenser. The gas absorber is a Fisher-Milligan scrubber (Fisher Catalog #07-513), or equivalent.
4. Spectrophotometer. Suitable for measurements at 578 nm with a 1.0-cm cell or larger.

#### 4.2 Materials

1. Potassium iodide-starch test paper.
2. Volumetric flasks, class A, 250 mL.

3. Volumetric flasks, class A, 100 mL.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Ascorbic acid ( $C_6H_8O_6$ ), analytical reagent grade crystals.
3. Bismuth nitrate solution ( $Bi(NO_3)_3$ ). Dissolve 30.0 grams of  $Bi(NO_3)_3$  in 100 mL of Type II water. While stirring, add 250 mL of glacial acetic acid. Stir until dissolved. Dilute to 1 liter with Type II water.
4. Chloramine-T solution. Dissolve 1.0 g of white, water-soluble, chloramine-T in 100 mL of Type II water. Refrigerate until ready to use.
5. Concentrated acetic acid ( $C_4H_6O_3$ ), glacial, reagent grade. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration  $<MDL$ , then the acid can be used.
6. Concentrated sulfuric acid ( $H_2SO_4$ ), reagent grade. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration  $<MDL$ , then the acid can be used.
7. Sulfuric acid (1:1). Slowly add 500 mL of concentrated  $H_2SO_4$  to 500 mL of Type II water.

**CAUTION:** This is an exothermic reaction.

8. Magnesium chloride solution ( $MgCl_2 \cdot 6H_2O$ ). Dissolve 510 g of  $MgCl_2 \cdot 6H_2O$  into a 1 liter flask. Dilute to 1 liter with Type II water.
9. Pyridine-barbituric acid reagent. Place 15 g of barbituric acid ( $C_4H_4O_3N_2$ ) in a 250 mL volumetric flask. Add just enough Type II water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine ( $C_5H_5N$ ) and mix. Add 15 mL of concentrated HCl. Allow to cool to room temperature. Dilute to 250 mL with Type II water. This reagent is stable for approximately six months, if stored in a cool, dark place.
10. Sodium dihydrogenphosphate ( $NaH_2PO_4 \cdot H_2O$ ), 1 M. Dissolve 138 g of  $NaH_2PO_4 \cdot H_2O$  in 1 liter of Type II water.
11. Sodium hydroxide solution (NaOH), 1.25 N. Dissolve 50 g of NaOH in Type II water. Dilute to 1 liter with Type II water.

12. Sulfamic acid solution ( $\text{NH}_2\text{SO}_3\text{H}$ ). Dissolve 40 g of sulfamic acid in Type II water. Dilute to 1 liter with Type II water.
13. Cyanide stock solution. Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of Type II water. Standardize with 0.0192 N  $\text{AgNO}_3$ . Dilute to appropriate concentration of 1 mg/mL.
14. Intermediate standard cyanide solution. Dilute 100.0 mL of stock cyanide solution to 1 liter with Type II water (100  $\mu\text{g}/\text{mL}$  CN).
15. Working standard cyanide solution. Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1 liter with Type II water (10.0  $\mu\text{g}/\text{mL}$  CN). Store in a glass-stoppered bottle.

**NOTE:** All working standards should contain 2 mL of 1 N NaOH per 100 mL.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Aqueous samples should be immediately preserved in the field by the addition of 10 N sodium hydroxide until the sample pH is  $\geq 12$ . A holding time of 14 days after sample collection is generally cited for this parameter.

Oxidizing agents, such as chlorine, decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with acidified potassium iodide (KI)-starch test paper as soon as the sample is collected. A blue color indicates the need for treatment. Add ascorbic acid a few crystals at a time until a drop of sample produces no color on the indicator. Then add an additional 0.6 g of ascorbic acid for each liter of water.

Samples should be stored under refrigerated conditions ( $4^\circ\text{C}$ ).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of aqueous samples to be analyzed for cyanide.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Two methods are given for preparing a standard cyanide curve. Section 7.1 should be followed if the samples do not contain sulfide and Section 7.2 should be followed if the samples to be analyzed contain sulfide. The difference between these two methods is that all the cyanide standards must be carried through the sample distillation process when sulfide is present.

### 7.1 Standard Curve for Samples without Sulfide.

1. Prepare a series of standards by pipetting suitable volumes of the working standard cyanide solution into 250 mL volumetric flasks. To each standard add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with Type II water. Prepare as follows:

<u>mL of Working Standard Solution</u> <u>(1 mL = 10 µg CN)</u>	<u>Concentration</u> <u>(µg CN/250 mL)</u>
0.0	BLANK
1.0	10
2.0	20
5.0	50
10.0	100
15.0	150
20.0	200

It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and a low) be distilled and compared with similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within  $\pm 10\%$  of the undistilled standards, the analyst should find the cause of the apparent error before proceeding.

2. Prepare a standard curve by plotting absorbances of standards vs. cyanide concentrations.

3. To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard cyanide solution or the working standard cyanide solution to 500 mL of sample to ensure a level of 20 µg/L. Proceed with the analysis as in Section 8.1 - Sample Distillation.

## 7.2 Standard Curve for Samples with Sulfide

1. All standards must be distilled in the same manner as the samples. A minimum of three standards shall be distilled.
2. Prepare a standard curve by plotting absorbance of standards vs. cyanide concentration.

## 8.0 Procedure

### 8.1 Sample Distillation

1. Place 500 mL of sample, or an aliquot diluted to 500 mL, in a 1 liter boiling flask.
2. Pipet 50 mL of 1.25 N sodium hydroxide solution into the absorbing tube of the reflux distillation apparatus. Connect the boiling flask, condenser, absorber, and trap in the train.
3. Adjust the vacuum source to allow a slow stream of air to enter the boiling flask. Approximately two bubbles of air per second should enter the boiling flask.
4. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper.

**NOTE:** If test is positive, treat the sample by adding 50 mL of bismuth nitrate solution through the air inlet tube after the air rate is set. Mix for 3 minutes prior to addition of H<sub>2</sub>SO<sub>4</sub> in step 6.

5. If samples are suspected to contain NO<sub>3</sub> and/or NO<sub>2</sub>, add 50 mL of sulfamic acid solution after the air rate is set through the air inlet tube. Mix for 3 min prior to addition of H<sub>2</sub>SO<sub>4</sub>.
6. Slowly add 50 mL 1:1 H<sub>2</sub>SO<sub>4</sub> through the air inlet tube.
7. Rinse the tube with Type II water and allow the airflow to mix the flask contents for 3 min.
8. Pour 20 mL of magnesium chloride into the air inlet and wash down with stream of water.

9. Heat the solution to boiling. Reflux for 1 hr. Turn off heat and continue the airflow for at least 15 min. After cooling the boiling flask, disconnect absorber and close off the vacuum source.
10. Drain the solution from the absorber into a 250 mL volumetric flask. Wash the absorber with Type II water and add the washings to the flask. Dilute to the 250 mL with Type II water. The sample is now ready for analysis.

## 8.2 Manual Spectrophotometric Analysis

1. Withdraw 50 mL, or a smaller aliquot diluted to 50 mL with 1.25 N sodium hydroxide solution, of the final sample distillate and transfer to a 100 mL volumetric flask.
2. Add 15.0 mL of sodium dihydrogenphosphate solution. Mix.
3. Add 2 mL of Chloramine-T. Mix.

**NOTE:** Some distillates may contain compounds that have a chlorine demand. One minute after the addition of chloramine-T, test for residual chlorine with KI-starch paper. If the test is negative, add an additional 0.5 mL chloramine-T. Recheck after 1 min.

**NOTE:** Temperature of reagents may affect the response factor of the colorimetric determination. The reagents stored under refrigerated conditions should be warmed to ambient temperature before use. Also, samples should not be left in a warm instrument to develop color but, instead, should be aliquoted to a cuvette immediately prior to reading the sample absorbance.

4. After 1 to 2 min, add 5 mL of pyridine-barbituric acid solution. Mix.
5. Dilute to 100 mL with Type II water. Mix.
6. Allow 8 min for color development and then read absorbance at 578 nm in a 1-cm cell within 15 min.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for cyanide in aqueous solutions is 5000 µg/L.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured cyanide concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the instrument detection limit.

### 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.6 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - cyanide, to the 100 mL aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The matrix spike should be prepared by adding cyanide from the working standard or intermediate cyanide standard to ensure a final concentration of approximately 40 µg/L. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within ± 15% of the known spike concentration. Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of ≤ 20%.

## 10.0 Method Performance

In a single laboratory (EMSL-CIN) test, using mixed industrial and domestic waste samples at concentrations of 0.06, 0.13, 0.28, and 0.62 mg/L CN, the precision standard deviations were ± 0.005, ± 0.007, ± 0.031, and ± 0.094, respectively.

In the same single laboratory (EMSL-CIN) test, using mixed industrial and domestic waste samples at 0.28 and 0.62 mg/L CN, the analyte recoveries were 85% and 102%, respectively.

## 11.0 Calculations and Reporting

The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences, such as those that contain sulfide (see section 11.1). The results of all other colorimetric analyses can be used to calculate the cyanide concentration in the original sample as follows:

$$\text{CN, } \mu\text{g/L} = \frac{(A \times 1,000) \times 50}{(B \times C)}$$

where:

A = CN read from standard curve, µg.

B = volume of original sample for distillation, mL.

C = volume taken for colorimetric analysis, mL.

## 11.1 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. Method 4500-CN C and 4500-CN E. 17th Edition, APHA, New York, New York. p. 4-29 - 4-31.

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# ARSENIC IN WATERS AND ELUTRIATES (ICP)

## 1.0 Scope and Application

Inductively coupled plasma atomic emission spectroscopy (ICP) determines arsenic and numerous other elements that are present in aqueous samples, such as surface water and elutriate samples. The aqueous samples must first be digested with nitric acid prior to analysis.

Detection limits, sensitivity, and optimum concentration ranges for arsenic, and other metals stable in a mixed standard solution with arsenic, will vary with the sample aliquot size, the spectrophotometer being used, and possible matrix interferences. The data shown in Table 1 provide concentration ranges for clean aqueous samples.

The method of standard addition (MSA) shall be used for the analysis of all sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required (see section 9).

This method should only be used by spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

This procedure is based on SW-846 Methods 3010 (for digestion) and 6010 for arsenic quantitation (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

Prior to analysis, the samples to be analyzed are refluxed with nitric acid in a covered beaker. This step is repeated with additional HNO<sub>3</sub> until the final digestate is light in color and diluted to volume.

This instrumental method measures light emitted by arsenic in the final digest by optical spectrometry. The digested samples are nebulized and the resulting aerosol is transported to a plasma torch. Arsenic-specific atomic-line

emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes.

Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

The possibility of additional interferences named in section 3.0 should also be recognized and appropriate corrections made when necessary. The procedures that can be used for this purpose are described in section 9.

### 3.0 Interferences

There are three main forms of interferences that can occur during the analysis of water and elutriate samples by ICP. These three types of interferences include: (1) spectral, (2) physical, and (3) chemical interferences. Each is discussed separately in the following sections.

#### 3.1 Spectral Interferences

Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multi-element instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended

as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferants can be assumed.

The magnitude of the interference effects summarized in Table 2 are expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of V. According to Table 2, 100 mg/L of V would yield a false signal for As equivalent to approximately 1.1 mg/L. Therefore, the presence of 10 mg/L of V would result in a false signal for As equivalent to approximately 0.11 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, and argon flow rate.

The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

### 3.2 Physical Interferences

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Further, it has been reported that better control of the argon flow rate improves instrument performance. Improved argon flow rate control can be accomplished with the use of mass flow controllers.

### 3.3 Chemical Interferences

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant

with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, etc.), buffering of the sample, matrix matching, and standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Centrifuge and centrifuge tubes.
4. Electric hot plate, adjustable and capable of maintaining a temperature of 90-95° C.
5. Inductively coupled argon plasma emission spectrometer.
6. Computer-controlled emission spectrometer with background correction.
7. Radio frequency generator.
8. Argon gas supply, welding grade or better.

### 4.2 Materials

1. Griffin beakers, 150 mL, or equivalent.
2. Watch glasses, ribbed and plain.
3. Whatman No. 41 filter paper, or equivalent.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
3. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.

4. Nitric acid (1:1). Add 500 mL concentrated  $\text{HNO}_3$  to 400 mL Type II water. Dilute to 1 liter with Type II water.
5. Hydrochloric acid (1:1). Add 500 mL concentrated  $\text{HCl}$  to 400 mL Type II water. Dilute to 1 liter with Type II water.
6. Standard stock solutions. May be purchased or prepared from ultrahigh purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hr at  $105^\circ\text{C}$ , unless otherwise specified.

**CAUTION:** Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

7. Arsenic standard stock solution, (100  $\mu\text{g}/\text{mL}$ ). Dissolve 0.13 g of  $\text{As}_2\text{O}_3$  weighed accurately to at least four significant figures, in 100 mL of Type II water containing 0.4 g  $\text{NaOH}$ . Acidify the solution with 2 mL concentrated  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
8. Molybdenum standard stock solution, (100  $\mu\text{g}/\text{mL}$ ). Dissolve 0.20 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ , weighed accurately to at least four significant figures, in Type II water. Dilute to 1 liter with Type II water.
9. Silica standard stock solution, (100  $\mu\text{g}/\text{mL}$ ). Do not dry. Dissolve 0.47 g  $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$ , weighed accurately to at least four significant figures, in Type II water. Add 10.0 mL concentrated  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
10. Mixed calibration standard solutions. Care should be taken when preparing mixed standards for ICP analysis to ensure that the elements in the final mixed standard are compatible and stable together. One set of mixed calibration standards that has been found to be useful is listed in Table 3. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities.

To prepare the mixed calibration standard for arsenic, combine appropriate volumes of the individual stock solutions indicated in Table 3 in volumetric flask. Add 2 mL 1:1  $\text{HNO}_3$  and 10 mL of 1:1  $\text{HCl}$  and dilute to 100 mL with Type II water. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see section 9.8) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should be scanned using a sequential spectrometer to verify

the absence of interelement spectral interference in the recommended mixed standard solutions.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Si
IV	Al, Ca, Cr, K, Na, and Ni

**NOTE:** Premixed standard solutions (traceable to NIST) containing the combined elements as listed in solutions I through IV are available from a number of commercial vendors.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Aqueous samples should be acidified to a pH of <2 with HNO<sub>3</sub>. A holding time of 6 months after sample collection is generally cited for this parameter.

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of aqueous samples to be analyzed for arsenic.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Prepare a calibration blank (see section 9.4.1) and at least three mixed calibration standards in the appropriate concentration range to correlate arsenic concentrations with the ICP's linear response range. Prepare standards for

instrument calibration as instructed in section 5.13. Match the sample matrix and that of the standards as closely as possible.

Calibrate the instrument according to the instrument manufacturer's recommended procedures using typical mixed calibration standard solutions. Flush the system with the calibration blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

## 8.0 Procedure

1. Transfer a 100 mL representative aliquot of the well-mixed aqueous sample to a 150 mL Griffin beaker.
2. Add 3 mL of concentrated  $\text{HNO}_3$ . Cover the beaker with a ribbed watch glass.
3. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL) making certain that the sample does not boil and that no portion of the beaker is allowed to go dry.

**NOTE:** If a sample is allowed to go to dryness, low recoveries may result. Should this occur, repeat the steps 1 through 3 with a fresh sample aliquot.

4. Cool the beaker and add 3 mL of concentrated  $\text{HNO}_3$ .
5. Cover the beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.
6. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing).
7. Uncover the beaker, or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker.
8. Add a small quantity of 1:1 HCl (10 mL/100 of final solution) and warm the beaker for an additional 15 min to dissolve any precipitate or residue resulting from evaporation.
9. Wash down the beaker walls and watch glass with Type II water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer.

**NOTE:** Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and the filtering apparatus are thoroughly cleaned and prerinsed with dilute  $\text{HNO}_3$ .

10. Adjust to the final volume of 100 mL with Type II water. The sample is now ready for analysis.
11. The analyst should follow the instructions provided by the instrument's manufacturer. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range where coordination factors are valid. The analyst must: (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.
12. Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this conditions.
13. Flush the system with the calibration blank solution for at least 1 min before the analysis of each sample. Analyze samples.

**NOTE:** Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for arsenic in aqueous solutions is 75 µg/L.

The method detection limit specified in this manual is sufficient to meet the Great Lakes Water Quality Criteria for arsenic (360 µg/l). For projects requiring more sensitive analyses of arsenic in waters and elutriates, a graphite furnace atomic absorption procedure has been provided in this methods appendix.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured arsenic concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance of the ICP and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Blanks

Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

#### 9.4.1 Calibration Blank

The calibration blank is prepared by diluting 2 mL of 1:1 HNO<sub>3</sub> and of 1:1 HCl to 100 mL with Type II water. Prepare a sufficient quantity to flush the system between standards and samples.

The calibration blank should be analyzed prior to routine sample analysis, after every 10 samples, and at the end of the analytical run. The measured concentration in the calibration blank should be less than or equal to the method detection limit.

#### 9.4.2 Reagent Blank

The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

### 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

### 9.6 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - arsenic, to the 100 mL aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and

analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have a relative percent difference (RPD) of  $\leq 20\%$ .

## 9.7 Interference Check Sample

The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the method detection limit for each element. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

The interference check sample should be analyzed at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Results should be within  $\pm 20\%$  of the known concentration.

## 9.8 Calibration Control Sample

A calibration control sample should be prepared in the same acid matrix as the calibration standards at 10 times the method detection limit. This sample should be prepared in accordance with the instructions provided by the supplier. The calibration control sample is used to verify the integrity of the calibration standards on a weekly basis.

## 9.9 Recommended Tests

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

### 9.9.1 Serial Dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the method detection limit after dilution), an analysis of a 1:4 dilution should

agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

### 9.9.2 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The

abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 10.0 Method Performance

In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was  $9 \pm 2\%$ . The mean percent recovery of spiked elements for all wastes was  $93 \pm 6\%$ . Spike levels ranged from 100  $\mu\text{g/L}$  to 100  $\text{mg/L}$ . The wastes included sludges and industrial wastewaters.

## 11.0 Calculations and Reporting

If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in  $\mu\text{g/L}$  with up to three significant figures.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

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Winge, R.K., V.J. Peterson, and V.A. Fassel. 1979. Inductively coupled plasma-atomic emission spectroscopy: Prominent lines, final report, March 1977 - February 1978, Ames laboratory, Ames, IA. EPA-600/4-79-017. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Table 1. Recommended Wavelengths and Estimated Instrumental Detection Limits.

Element	Wavelength <sup>a</sup> (nm)	Estimated Detection Limit <sup>b</sup> (µg/L)
Arsenic	193.696	53
Molybdenum	202.030	8
Silicon	288.158	58

a - The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see section 3.1).

b - The estimated instrumental detection limits are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

Table 2. Analyte Concentration Equivalents arising from Interference at the 100 mg/L Level.

Analyte	Wavelength (nm)	Interferant <sup>a,b</sup>									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Mo	Tl	V
Arsenic	193.696	1.3	-	0.44	-	-	-	-	-	-	1.1
Molybdenum	202.030	0.05	-	-	-	0.03	-	-	-	-	-
Silicon	288.158	-	-	0.07	-	-	-	-	-	-	0.01

a - Dashes indicate that no interference was observed even when interferants were introduced at the following levels:

Al - 1000 mg/L,	Mg - 1000 mg/L,
Ca - 1000 mg/L,	Mn - 200 mg/L,
Cr - 200 mg/L,	Tl - 200 mg/L,
Cu - 200 mg/L,	V - 200 mg/L, and
Fe - 1000 mg/L.	

b - The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

Table 4. ICP Precision and Accuracy Data<sup>a</sup>

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)
As	200	208	7.5	22	19	23	60	63	17

a - Not all elements were analyzed by all laboratories.

b - SD = standard deviation.

# ARSENIC IN WATERS AND ELUTRIATES (GFAA)

## 1.0 Scope and Application

This method is an atomic absorption procedure suitable for the determination of arsenic in natural water samples and mobility extracts such as sediment elutriates. All samples must be subjected to an acid digestion/oxidation step prior to analysis.

This procedure is based on EPA SW-846 Method 7060 (USEPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

Prior to analysis, samples are treated with a mixture of hydrogen peroxide and nitric acid in order to convert organic forms of arsenic to inorganic forms and minimize organic interferences.

Following sample pretreatment, a representative aliquot is spiked with a nickel nitrate solution and placed into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode or EDL radiation during sample atomization is proportional to the arsenic concentration.

## 3.0 Interferences

Elemental arsenic and many of its compounds are volatile; therefore, samples may be subject to potential loss of arsenic during sample preparation. Spiked samples and relevant standard reference materials should be processed to determine if the analytical procedure is performing adequately.

Caution should also be employed when selecting the temperature and duration of the sample drying and charring (ashing) cycles. A nickel nitrate solution must be added to all prepared samples prior to analysis to minimize volatilization losses during drying and ashing.

In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Simultaneous background correction must be employed to avoid erroneously high results. Aluminum is a severe positive interferant in the analysis of arsenic, especially using D<sub>2</sub> arc background correction. Zeeman background correction is very useful in this situation.

If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected by means of blank burns, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, 3-5 weights covering expected weight range.
3. Electric hot plate, adjustable and capable of maintaining a temperature of 90-95° C.
4. Thermometer, 0 to 100° C range.
5. Atomic absorption spectrophotometer, single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip-chart recorder.
6. Arsenic hollow cathode lamp, or electrodeless discharge lamp (EDL). EDLs are recommended since they provide better sensitivity for arsenic analyses.
7. Graphite furnace. Any graphite furnace device with the appropriate temperature and timing controls.
8. Strip-chart recorder. A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, and changes in sensitivity can easily be recognized.

## 4.2 Materials

1. Griffin beakers, 250 mL, or equivalent.
2. Volumetric flasks, class A, 10 mL.
3. Volumetric flasks, class A, 50 mL.
4. Pipets. Microliter with disposable tips. Sizes can range from 5 to 1,000  $\mu\text{L}$ , as required.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated nitric acid, reagent grade ( $\text{HNO}_3$ ). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid is  $<\text{MDL}$ , then the acid can be used.
3. Hydrogen peroxide, 30% ( $\text{H}_2\text{O}_2$ ). Oxidant should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the  $\text{H}_2\text{O}_2$  is  $<\text{MDL}$ , then the acid can be used.
4. Arsenic standard stock solution (1,000 mg/L). Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide ( $\text{As}_2\text{O}_3$ , analytical reagent grade), or equivalent, in 100 mL of Type II water containing 4 g NaOH. Acidify the solution with 20 mL concentrated  $\text{HNO}_3$  and dilute to 1 liter (1 mg/mL As).
5. Nickel nitrate solution, 5%. Dissolve 24.780 g of ACS reagent grade  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , or equivalent, in Type II water and dilute to 100 mL.
6. Nickel nitrate solution, 1%. Dilute 20 mL of the 5% nickel nitrate to 100 mL with Type II water.
7. Arsenic working standards. Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquot of the stock solution, add 1 mL of concentrated  $\text{HNO}_3$ , 2 mL of 30%  $\text{H}_2\text{O}_2$ , and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with Type II water.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Water and elutriate samples should be acidified to a pH <2 with HNO<sub>3</sub>. A holding time of 6 months is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of samples to be analyzed for arsenic in sediments.

**NOTE:** Special containers (e.g., containers used for volatile organic analysis) may have to be used if the samples are to be analyzed for very volatile arsenic compounds.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^\circ \text{C}$ .

The hot plate should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^\circ \text{C}$ .

Prepare a method blank and at least three standards in the appropriate concentration range to correlate arsenic concentrations with the atomic absorption spectrophotometer's linear response range. Prepare standards for instrument calibration by appropriate dilution of the stock arsenic solution. These standards should be prepared fresh on the day of use. Match the sample matrix and that of the standards as closely as possible.

Inject a suitable portion of each standard into the graphite furnace in order of increasing concentration. It is recommended that each standard solution be

analyzed in triplicate in order to assess method precision. Instrument calibration curves should be composed of a minimum of a blank and three standards. A calibration curve should be prepared every day of continuous sample analysis and prior to the initiation of the project's routine sample analysis.

Construct an analytical curve by plotting the average peak absorbance or peak area for the standard solutions as a function of sample concentration on a linear graph. Prepare this graph daily when new initial calibration information is obtained. Alternatively, electronic instrument calibration can be used if the instrument is appropriately equipped.

## 8.0 Procedure

1. Transfer 100 mL of well-mixed sample to a 250 mL Griffin beaker.
2. Add 2 mL of 30% H<sub>2</sub>O<sub>2</sub> and sufficient concentrated HNO<sub>3</sub> to result in an acid concentration of 1% (v/v).
3. Heat for 1 hr at 95° C or until the volume is slightly less than 50 mL.
4. Cool the digested sample. Quantitatively transfer the sample to a 50 mL volumetric flask and dilute to a 50 mL volume with Type II water.
5. Pipet 5 mL of the digested solution into a 10-mL volumetric flask.
6. Add 1 mL of the 1% nickel nitrate solution and dilute to 10 mL with Type II water. The sample is now ready for injection into the furnace.
7. The 193.7 nm wavelength line and a background correction system are required. Follow the manufacturer's suggestions for all other spectrophotometer parameters.
8. Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.
9. Inject a measured microliter (μL) aliquot of sample digest into the furnace and atomize. If the digest concentration is greater than the highest standard, or if the instrument response falls on the plateau of the calibration curve, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for arsenic in waters and elutriates is 75 µg/L.

The method detection limit specified in this manual is sufficient to meet the Great Lakes Water Quality Criteria for arsenic (360 µg/l).

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured arsenic concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standard 1643c - Water, should be run to monitor the life and performance of the graphite tube and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a water sample, prepared by spiking ASTM Type II water at the laboratory, and that has undergone multiple analyses by the analytical laboratory. The lot numbers of the As stock solution used in the creation of the LCS should be different from those used to prepare the calibration (both initial and ongoing) standards. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

## 9.5 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the instrument detection limit.

## 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 15 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.7 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - arsenic, to the 100 mL sample aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 3 times the estimated or actual method detection limit. The added matrix spike should have a negligible volume when compared to the routine sample volume to eliminate/control sample dilution effects. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 20\%$ .

## 10.0 Method Performance

The optimal concentration range for this method is 5-100  $\mu\text{g/L}$ .

Data summarized in Table 1 provide an estimate of the precision that can be obtained with the method (APHA, 1989).

## 11.0 Calculations and Reporting

Calculate metal concentrations by (1) the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account.

The method of standard additions is the preferred method for the analysis of all sediment elutriates to compensate for any sample matrix effects.

Prepare a standard curve based on the absorbance and concentration of the arsenic standards. Determine the arsenic concentration in each of the sediment digests by comparing the digest absorbance with the standard calibration curve.

Arsenic concentrations in water or elutriate samples should be reported in  $\mu\text{g/L}$ .

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. 17th Edition, APHA, New York, New York.

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Table 1. Method Performance Data for Arsenic by Electrothermal Atomization (APHA, 1989).

Single-Analyst Precision, % RSD					
Concentration µg/L	Lab Water	Drinking Water	Surface Water	Effluent 1	Effluent 2
9.78	40	25	15	74	23
227	10	6	8	11	15

Interlaboratory Precision, % RSD					
Concentration µg/L	Lab Water	Drinking Water	Surface Water	Effluent 1	Effluent 2
9.78	43	26	37	72	50
227	18	12	13	20	15

Interlaboratory Relative Error, %					
Concentration µg/L	Lab Water	Drinking Water	Surface Water	Effluent 1	Effluent 2
9.78	43	26	37	72	50
9.78	36	1	22	106	13
227	3	7	10	19	6

# CADMIUM IN WATERS AND ELUTRIATES (ICP)

## 1.0 Scope and Application

Inductively coupled plasma atomic emission spectroscopy (ICP) determines cadmium and numerous other elements that are present in aqueous samples, such as surface water and elutriate samples. The aqueous samples must first be digested with nitric acid prior to analysis.

Detection limits, sensitivity, and optimum concentration ranges for cadmium, and other metals stable in a mixed standard solution with cadmium, will vary with the sample aliquot size, the spectrophotometer being used, and possible matrix interferences. The data shown in Table 1 provide concentration ranges for clean aqueous samples.

The method of standard addition (MSA) shall be used for the analysis of all sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required (see section 9).

This method should only be used by spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

This procedure is based on SW-846 Methods 3010 (for digestion) and 6010 for quantitation (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" to waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

Prior to analysis, the samples to be analyzed are refluxed with nitric acid in a covered beaker. This step is repeated with additional HNO<sub>3</sub> until the final digestate is light in color and diluted to volume.

This instrumental method measures light emitted by cadmium in the final digest by optical spectrometry. The digested samples are nebulized and the resulting aerosol is transported to a plasma torch. Cadmium-specific atomic-line

emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes.

Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

The possibility of additional interferences named in section 3.0 should also be recognized and appropriate corrections made when necessary. The procedures that can be used for this purpose are described in section 9.

### 3.0 Interferences

There are three main forms of interferences that can occur during the analysis of water and elutriate samples by ICP. These three types of interferences include: (1) spectral, (2) physical, and (3) chemical interferences. Each is discussed separately in the following sections.

#### 3.1 Spectral Interferences

Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multi-element instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended

as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferants can be assumed.

The magnitude of the interference effects summarized in Table 2 are expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that Cd is to be determined (at 226.502 nm) in a sample containing approximately 10 mg/L of Fe. According to Table 2, 100 mg/L of Fe would yield a false signal for Cd equivalent to approximately 0.03 mg/L. Therefore, the presence of 10 mg/L of Fe would result in a false signal for Cd equivalent to approximately 0.003 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, and argon flow rate.

The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

### 3.2 Physical Interferences

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Further, it has been reported that better control of the argon flow rate improves instrument performance. Improved argon flow rate control can be accomplished with the use of mass flow controllers.

### 3.3 Chemical Interferences

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant

with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, etc.), buffering of the sample, matrix matching, and standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Centrifuge and centrifuge tubes.
4. Electric hot plate, adjustable and capable of maintaining a temperature of 90-95° C.
5. Inductively coupled argon plasma emission spectrometer.
6. Computer-controlled emission spectrometer with background correction.
7. Radio frequency generator.
8. Argon gas supply, welding grade or better.

### 4.2 Materials

1. Griffin beakers, 150 mL, or equivalent.
2. Watch glasses, ribbed and plain.
3. Whatman No. 41 filter paper, or equivalent.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
3. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.

- Nitric acid (1:1). Add 500 mL concentrated  $\text{HNO}_3$  to 400 mL Type II water. Dilute to 1 liter with Type II water.
- Hydrochloric acid (1:1). Add 500 mL concentrated  $\text{HCl}$  to 400 mL Type II water. Dilute to 1 liter with Type II water.
- Standard stock solutions. May be purchased or prepared from ultrahigh purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hr at  $105^\circ\text{C}$ , unless otherwise specified.

**CAUTION:** Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

- Beryllium standard stock solution (100  $\mu\text{g}/\text{mL}$ ). Dissolve 1.970 g  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  (analytical reagent grade, undried), in 100 mL of Type II water, add 10.0 ml concentrated  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
- Cadmium standard stock solution (100  $\mu\text{g}/\text{mL}$ ). Dissolve 0.1100 g  $\text{CdO}$  (analytical reagent grade) in a minimum amount of 1:1  $\text{HNO}_3$ . Heat to increase rate of dissolution. Add 10.0 mL concentrated  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
- Lead standard stock solution (100  $\mu\text{g}/\text{mL}$ ). Dissolve 0.1600 g  $\text{Pb}(\text{NO}_3)_2$  (analytical reagent grade) in a minimum amount of 1:1  $\text{HNO}_3$ . Add 10 mL 1:1  $\text{HNO}_3$ . Add 10 mL 1:1  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
- Manganese standard stock solution (100  $\mu\text{g}/\text{mL}$ ). Dissolve 0.1000 g of manganese metal, in an acid mixture of 10 mL concentrated  $\text{HCl}$  and 1 mL concentrated  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
- Selenium standard stock solution (100  $\mu\text{g}/\text{mL}$ ). Dissolve 0.1700 g  $\text{H}_2\text{SeO}_3$  (analytical reagent grade, undried) in 100 mL of Type II water. Dilute to 1 liter with Type II water.
- Zinc standard stock solution (100  $\mu\text{g}/\text{mL}$ ). Dissolve 0.1200 g  $\text{ZnO}$  in a minimum amount of 1:1  $\text{HNO}_3$ . Add 10.0 mL concentrated  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
- Mixed calibration standard solutions. Care should be taken when preparing mixed standards for ICP analysis to ensure that the elements in the final mixed standard are compatible and stable together. One set of mixed calibration standards that has been found to be useful is listed in Table 3. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities.

To prepare the mixed calibration standard for cadmium, combine appropriate volumes of the individual stock solutions indicated in Table

3 in volumetric flask. Add 2 mL 1:1 HNO<sub>3</sub> and 10 mL of 1:1 HCl and dilute to 100 mL with Type II water. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see section 9.8) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Si
IV	Al, Ca, Cr, K, Na, and Ni

**NOTE:** Premixed standard solutions (traceable to NIST) containing the combined elements as listed in solutions I through IV are available from a number of commercial vendors.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Aqueous samples should be acidified to a pH of <2 with HNO<sub>3</sub>. A holding time of 6 months after sample collection is generally cited for this parameter.

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of aqueous samples to be analyzed for cadmium.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Prepare a calibration blank (see section 9.4.1) and at least three mixed calibration standards in the appropriate concentration range to correlate cadmium concentrations with the ICP's linear response range. Prepare standards for instrument calibration as instructed in section 5.13. Match the sample matrix and that of the standards as closely as possible.

Calibrate the instrument according to the instrument manufacturer's recommended procedures using typical mixed calibration standard solutions. Flush the system with the calibration blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

## 8.0 Procedure

1. Transfer a 100 mL representative aliquot of the well-mixed aqueous sample to a 150 mL Griffin beaker.
2. Add 3 mL of concentrated  $\text{HNO}_3$ . Cover the beaker with a ribbed watch glass.
3. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL) making certain that the sample does not boil and that no portion of the beaker is allowed to go dry.

**NOTE:** If a sample is allowed to go to dryness, low recoveries may result. Should this occur, repeat the steps 1 through 3 with a fresh sample aliquot.

4. Cool the beaker and add 3 mL of concentrated  $\text{HNO}_3$ .
5. Cover the beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.
6. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing).

7. Uncover the beaker, or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker.
8. Add a small quantity of 1:1 HCl (10 mL/100 of final solution) and warm the beaker for an additional 15 min to dissolve any precipitate or residue resulting from evaporation.
9. Wash down the beaker walls and watch glass with Type II water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer.

**NOTE:** Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and the filtering apparatus are thoroughly cleaned and prerinsed with dilute  $\text{HNO}_3$ .

10. Adjust to the final volume of 100 mL with Type II water. The sample is now ready for analysis.
11. The analyst should follow the instructions provided by the instrument's manufacturer. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range where coordination factors are valid. The analyst must: (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.
12. Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this conditions.
13. Flush the system with the calibration blank solution for at least 1 min before the analysis of each sample. Analyze samples.

**NOTE:** Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for cadmium in aqueous solutions is 4 µg/L.

The method detection limit specified in this method is insufficient to meet the Great Lakes Water Quality Criteria for cadmium (2.1 µg/L). However, this method has been presented to allow for the use of the ICP as a screening tool for cadmium. If the measured concentrations are greater than 4 µg/L, the Great Lakes Water Quality Criteria has been violated and no further analyses are needed. However, if the measured concentration is below 4 µg/L, cadmium must be quantified using the graphite furnace atomic absorption procedure presented in this appendix.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured cadmium concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance of the ICP and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be ± 15% of the known value or within the certified value provided by the supplier, whichever is larger.

## 9.4 Blanks

Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

### 9.4.1 Calibration Blank

The calibration blank is prepared by diluting 2 mL of 1:1 HNO<sub>3</sub> and of 1:1 HCl to 100 mL with Type II water. Prepare a sufficient quantity to flush the system between standards and samples.

The calibration blank should be analyzed prior to routine sample analysis, after every 10 samples, and at the end of the analytical run. The measured concentration in the calibration blank should be less than or equal to the method detection limit.

### 9.4.2 Reagent Blank

The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.6 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - cadmium, to the 100 mL aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have a relative percent difference (RPD) of  $\leq 20\%$ .

## 9.7 Interference Check Sample

The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the method detection limit for each element. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

The interference check sample should be analyzed at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Results should be within  $\pm 20\%$  of the known concentration.

## 9.8 Calibration Control Sample

A calibration control sample should be prepared in the same acid matrix as the calibration standards at 10 times the method detection limit. This sample should be prepared in accordance with the instructions provided by the supplier. The calibration control sample is used to verify the integrity of the calibration standards on a weekly basis.

## 9.9 Recommended Tests

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests will ensure the analyst that neither positive nor

negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

### 9.9.1 Serial Dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the method detection limit after dilution), an analysis of a 1:4 dilution should agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

### 9.9.2 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 10.0 Method Performance

In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was  $9 \pm 2\%$ . The mean percent recovery of spiked elements for all wastes was  $93 \pm 6\%$ . Spike levels ranged from 100  $\mu\text{g/L}$  to 100  $\text{mg/L}$ . The wastes included sludges and industrial wastewaters.

## 11.0 Calculations and Reporting

If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in  $\mu\text{g/L}$  with up to three significant figures.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Winge, R.K., V.J. Peterson, and V.A. Fassel. 1979. Inductively coupled plasma-atomic emission spectroscopy: Prominent lines, final report, March 1977 - February 1978, Ames laboratory, Ames, IA. EPA-600/4-79-017. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Table 1. Recommended Wavelengths and Estimated Instrumental Detection Limits.

Element	Wavelength <sup>a</sup> (nm)	Estimated Detection Limit <sup>b</sup> (µg/L)
Beryllium	313.042	0.3
Cadmium	226.502	4
Lead	220.353	42
Manganese	257.610	2
Selenium	196.026	75
Zinc	213.856	2

a - The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see section 3.1).

b - The estimated instrumental detection limits are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

Table 2. Analyte Concentration Equivalentents arising from Interference at the 100 mg/L Level.

Analyte	Wavelength (nm)	Interferant <sup>a,b</sup>									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Mi	TI	V
Beryllium	313.042	-	-	-	-	-	-	-	-	0.04	0.05
Cadmium	226.502	-	-	-	-	0.03	-	-	0.02	-	-
Lead	220.353	0.17	-	-	-	-	-	-	-	-	-
Manganese	257.610	0.005	-	0.01	-	0.002	0.002	-	-	-	-
Selenium	196.026	0.23	-	-	-	0.09	-	-	-	-	-
Zinc	213.856	-	-	-	0.14	-	-	-	0.29	-	-

a - Dashes indicate that no interference was observed even when interferants were introduced at the following levels:

Al - 1000 mg/L,  
 Ca - 1000 mg/L,  
 Cr - 200 mg/L,  
 Cu - 200 mg/L,  
 Fe - 1000 mg/L,  
 Mg - 1000 mg/L,  
 Mn - 200 mg/L,  
 TI - 200 mg/L,  
 V - 200 mg/L, and

b - The figures recorded as analyte concentrations are not the actual observed concentrations. To obtain those figures, add the listed concentration to the interferant figure.

Table 4. ICP Precision and Accuracy Data<sup>a</sup>

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
Cd	50	48	12	2.5	2.9	16	14	13	16
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se <sup>c</sup>	40	32	21.9	6	8.5	42	10	8.5	8.3

a - Not all elements were analyzed by all laboratories.

b - SD = standard deviation.

c - Results for Se are from two laboratories.

# CADMIUM IN WATERS AND ELUTRIATES (GFAA)

## 1.0 Scope and Application

This method is an graphite furnace atomic absorption (GFAA) procedure suitable for the determination of cadmium in natural water samples and mobility extracts such as sediment elutriates. All samples must be subjected to an acid digestion step prior to analysis.

This procedure is based on EPA SW-846 Methods 3020 for sample digestion and 7131 for cadmium quantitation (USEPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

A mixture of nitric acid and the sample to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is cooled and brought up in dilute nitric acid such that the final dilution contains 3% (v/v) HNO<sub>3</sub>. If the sample contains suspended solids, it must be centrifuged, filtered, or allowed to settle.

Following sample digestion, a representative aliquot is slowly evaporated to dryness, charred (ashed), and atomized in a graphite furnace. The absorption of hollow cathode or EDL radiation during sample atomization is proportional to the cadmium concentration.

## 3.0 Interferences

The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference, the serial dilution technique (see section 9.8.1) may be used. Those samples which indicate the presence of interference should be treated in one or more of the following ways:

1. Successively dilute and reanalyze the samples to eliminate interferences.
2. Modify the sample matrix either to remove interferences or to stabilize the analyte. Examples are the addition of ammonium nitrate to remove alkali chlorides and the addition of ammonium phosphate to retain cadmium. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.
3. Analyze the sample by method of standard additions while noticing the precautions and limitations of its use (see section 9.8.2).

Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, use either background correction or choose an alternate wavelength. Background correction may also compensate for nonspecific broad-band absorption interference.

Continuum background correction cannot correct for all types of background interference. When the background interference cannot be compensated for, chemically remove the analyte or use an alternate form of background correction, e.g., Zeeman background correction.

Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analyte.

Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Interference can also occur when resonant energy from another element in a multielement lamp, or from a metal impurity in the lamp cathode, falls within the bandpass of the slit setting when that other metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

Cross-contamination and contamination of the sample can be major sources of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in the Materials section (section 4.2). Pipet tips are

a frequent source of contamination. Many yellow plastic tips contain cadmium. Use "cadmium-free" tips. If other pipet tips are suspected of causing sample contamination, they should be acid soaked with 1:5 HNO<sub>3</sub> and rinsed thoroughly with tap and Type II water. The use of a better grade of pipet tip can greatly reduce this problem.

Pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five to ten high-temperature burns may be required to clean the tube before use.

In addition to the normal interferences experienced during graphite furnace analysis, cadmium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Cadmium analysis is particularly susceptible to these problems because of its low analytical wavelength (228.8 nm). Simultaneous background correction must be employed to avoid erroneously high results.

Excess chloride may cause premature volatilization of cadmium. Ammonium phosphate used as a matrix modifier minimizes this loss.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Electric hot plate, adjustable and capable of maintaining a temperature of 90-95° C.
4. Thermometer, 0 to 100° C range.
5. Atomic absorption spectrophotometer, single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip-chart recorder.
6. Cadmium hollow cathode lamp, or electrodeless discharge lamp (EDL).
7. Graphite furnace. Any graphite furnace device with the appropriate temperature and timing controls.

8. Strip-chart recorder. A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, and changes in sensitivity can easily be recognized.

## 4.2 Materials

1. Commercial grade available argon and nitrogen are required for furnace work.
2. Griffin beakers, 150 mL, or equivalent.
3. Volumetric flasks, class A, 1 L.
4. Volumetric flasks, class A, 100 mL.
5. Pipets. Microliter with disposable tips. Sizes can range from 5 to 100  $\mu\text{L}$ , as required.

**NOTE:** All glassware, polypropylene, or Teflon containers, including sample bottles, should be washed in the following sequence: detergent, tap water, 1:1  $\text{HNO}_3$ , tap water, 1:1  $\text{HCl}$ , tap water, and Type II water.

**NOTE:** Chromic acid ( $\text{H}_2\text{CrO}_4$ ) should not be used as a cleaning agent for glassware if chromium is to be included in the analytical scheme for the sample digestate.

6. Watch glass, ribbed. Watch glass should be large enough to cover the mouth of the beaker.
7. Watch glass, non-ribbed. Watch glass should be large enough to cover the mouth of the beaker.

## 5.0 Reagents

1. Ammonium phosphate solution ( $\text{NH}_4$ )<sub>2</sub> $\text{HPO}_4$ ), analytical reagent grade, 40%. Dissolve 40 g of  $\text{NH}_4$ )<sub>2</sub> $\text{HPO}_4$  in 50 mL of Type II water. Dilute to 100 mL with Type II water.
2. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
3. Concentrated hydrochloric acid ( $\text{HCl}$ ), spectrograde grade certified for AA use. Acid should be analyzed to verify that contaminants are not

- present at levels that will interfere with method performance. If a method blank using the acid is <MDL, then the acid can be used.
4. Hydrochloric acid solution (HCl), 1:1. Add 500 mL of concentrated HCl to 400 mL of Type II water. Dilute to 1 liter with Type II water.
  5. Concentrated nitric acid (HNO<sub>3</sub>), spectrograde grade certified for AA use. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid is <MDL, then the acid can be used.
  6. Nitric acid solution (HNO<sub>3</sub>), 1:1. Add 500 mL of concentrated HNO<sub>3</sub> to 400 mL of Type II water. Dilute to 1 liter with Type II water.
  7. Cadmium standard stock solution (1,000 mg/L). Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.000 g of cadmium metal, analytical reagent grade, in 20 mL of 1:1 HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
  8. Cadmium working standards. Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. To each 100 mL of standard, add 2 mL of ammonium phosphate solution. The calibration standard should be prepared to contain 0.5% (v/v) HNO<sub>3</sub>.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Water and elutriate samples should be acidified to a pH <2 with HNO<sub>3</sub>. A holding time of 6 months is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water (see note in section 4.2). Either glass or plastic containers can be used for the storage of samples to be analyzed for cadmium in aqueous samples.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^\circ \text{C}$ .

The hot plate should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^\circ \text{C}$ .

Prepare a method blank and at least three standards in the appropriate concentration range to correlate cadmium concentrations with the atomic absorption spectrophotometer's linear response range. Prepare standards for instrument calibration by appropriate dilution of the cadmium standard stock solution. These standards should be prepared fresh on the day of use. Match the sample matrix and that of the standards as closely as possible.

Inject a suitable portion of each standard into the graphite furnace in order of increasing concentration. It is recommended that each standard solution be analyzed in triplicate in order to assess method precision. Instrument calibration curves should be composed of a minimum of a blank and three standards. A calibration curve should be prepared every day of continuous sample analysis and prior to the initiation of the project's routine sample analysis.

Construct an analytical curve by plotting the average peak absorbance or peak area for the standard solutions as a function of sample concentration on a linear graph. Prepare this graph daily when new initial calibration information is obtained. Alternatively, electronic instrument calibration can be used if the instrument is appropriately equipped.

## 8.0 Procedure

### 8.1 Sample Preparation

1. Transfer 100 mL of well mixed sample to a 150 mL Griffin beaker.
2. Add 3 mL of concentrated  $\text{HNO}_3$ .
3. Cover the beaker with a ribbed watch glass.

4. Place the beaker on a hot plate and cautiously evaporate to a low volume (approximately 5 mL) making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry.
5. Cool the digested sample and add 3 mL of concentrated HNO<sub>3</sub>.
6. Cover the beaker with a non-ribbed watch glass.
7. Place the beaker on a hot plate and increase the temperature so that a gentle reflux action occurs.
8. Continue heating, adding additional acid as necessary, until the digestion is complete.

**NOTE:** Complete digestion is generally indicated by a light digestate color or if the digestate does not change in appearance with continued refluxing.

9. When the digestion is complete, cover with a ribbed watch glass and evaporate to a low volume (approximately 3 mL).

**NOTE:** Do not allow any portion of the beaker bottom to go dry.

10. Add approximately 10 mL of Type II water and mix.
11. Continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.
12. Remove beaker from hot plate and wash down the beaker walls and watch glass with Type II water.

**NOTE:** It may be necessary to filter or centrifuge the sample to remove silicates and other insoluble material that may interfere with injecting the sample into the graphite furnace.

13. Adjust the final volume to 100 mL with Type II water.
14. Add 2 mL of ammonium phosphate solution to each sample. The sample is now ready for analysis.

## 8.2 Sample Analysis

1. The 228.8 nm wavelength line and a background correction system are required. Follow the manufacturer's suggestions for all other spectrophotometer parameters.
2. Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing

mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

3. Inject a measured microliter ( $\mu\text{L}$ ) aliquot of sample digest into the furnace and atomize. If the digest concentration is greater than the highest standard, or if the instrument response falls on the plateau of the calibration curve, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for cadmium in waters and elutriates is  $1 \mu\text{g/L}$ .

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured cadmium concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standard 1643c - Water, should be run to monitor the life and performance of the graphite tube and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

## 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a water sample, prepared by spiking ASTM Type II water at the laboratory, and that has undergone multiple analyses by the analytical laboratory. The lot numbers of the As stock solution used in the creation of the LCS should be different from those used to prepare the calibration (both initial and ongoing) standards. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

## 9.5 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 15 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.7 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - cadmium, to the 100 mL sample aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 3 times the estimated or actual method detection limit. The added matrix spike should have a negligible volume when compared to the routine sample volume to eliminate/control sample dilution effects. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 20\%$ .

## 9.8 Recommended Tests

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values. Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition may be used (see Section 9.8.2).

### 9.8.1 Serial Dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the method detection limit after dilution), an analysis of a 1:4 dilution should agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

### 9.8.2 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through

the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 10.0 Method Performance

The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.5-10 µg/L.  
Detection limit: 0.1 µg/L.

Precision and accuracy data shown in Table 1 were obtained from records of state and contractor laboratories (USEPA, 1979).

## 11.0 Calculations and Reporting

Calculate metal concentrations by (1) the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account.

The method of standard additions is the preferred method for the analysis of all sediment elutriates to compensate for any sample matrix effects.

Prepare a standard curve based on the absorbance and concentration of the cadmium standards. Determine the cadmium concentration in each of the sample digests by comparing the digest absorbance with the standard calibration curve.

If dilution of sample was required, the following formula is provided to account for the dilution:

$$\text{Cd, } \mu\text{g/L} = \frac{A \times (B + C)}{C}$$

where:

A = metal in diluted aliquot from calibration curve,  $\mu\text{g/L}$ .

B = acid blank matrix used for dilution, mL.

C = sample aliquot, mL.

Cadmium concentrations in water or elutriate samples should be reported in  $\mu\text{g/L}$ .

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. 17th Edition, APHA, New York, New York.

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Table 1. Method Performance Data.

Number of Labs	True Value µg/L	Mean Value µg/L	Standard Deviation µg/L	Accuracy as % Bias
74	71	70	21	-2.2
73	78	74	18	-5.7
63	14	16.8	11.0	19.8
68	18	18.3	10.3	1.9
55	1.4	3.3	5.0	135
51	2.8	2.9	2.8	4.7

# CHROMIUM IN WATERS AND ELUTRIATES (ICP)

## 1.0 Scope and Application

Inductively coupled plasma atomic emission spectroscopy (ICP) determines chromium and numerous other elements that are present in aqueous samples, such as surface water and elutriate samples. The aqueous samples must first be digested with nitric acid prior to analysis.

Detection limits, sensitivity, and optimum concentration ranges for chromium, and other metals stable in a mixed standard solution with chromium, will vary with the sample aliquot size, the spectrophotometer being used, and possible matrix interferences. The data shown in Table 1 provide concentration ranges for clean aqueous samples.

The method of standard addition (MSA) shall be used for the analysis of all sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required (see section 9).

This method should only be used by spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

This procedure is based on SW-846 Methods 3010 (for digestion) and 6010 for quantitation (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

Prior to analysis, the samples to be analyzed are refluxed with nitric acid in a covered beaker. This step is repeated with additional HNO<sub>3</sub> until the final digestate is light in color and diluted to volume.

This instrumental method measures light emitted by chromium in the final digest by optical spectrometry. The digested samples are nebulized and the resulting aerosol is transported to a plasma torch. Chromium-specific atomic-line

emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes.

Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

The possibility of additional interferences named in section 3.0 should also be recognized and appropriate corrections made when necessary. The procedures that can be used for this purpose are described in section 9.

### 3.0 Interferences

There are three main forms of interferences that can occur during the analysis of water and elutriate samples by ICP. These three types of interferences include: (1) spectral, (2) physical, and (3) chemical interferences. Each is discussed separately in the following sections.

#### 3.1 Spectral Interferences

Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multi-element instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended

as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferants can be assumed.

The magnitude of the interference effects summarized in Table 2 are expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that Cd is to be determined (at 267.716 nm) in a sample containing approximately 10 mg/L of Mn. According to Table 2, 100 mg/L of Mn would yield a false signal for Cr equivalent to approximately 0.04 mg/L. Therefore, the presence of 10 mg/L of Mn would result in a false signal for Cr equivalent to approximately 0.004 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, and argon flow rate.

The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

### 3.2 Physical Interferences

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Further, it has been reported that better control of the argon flow rate improves instrument performance. Improved argon flow rate control can be accomplished with the use of mass flow controllers.

### 3.3 Chemical Interferences

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant

with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, etc.), buffering of the sample, matrix matching, and standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Centrifuge and centrifuge tubes.
4. Electric hot plate, adjustable and capable of maintaining a temperature of 90-95° C.
5. Inductively coupled argon plasma emission spectrometer.
6. Computer-controlled emission spectrometer with background correction.
7. Radio frequency generator.
8. Argon gas supply, welding grade or better.

### 4.2 Materials

1. Griffin beakers, 150 mL, or equivalent.
2. Watch glasses, ribbed and plain.
3. Whatman No. 41 filter paper, or equivalent.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
3. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.

- Nitric acid (1:1). Add 500 mL concentrated  $\text{HNO}_3$  to 400 mL Type II water. Dilute to 1 liter with Type II water.
- Hydrochloric acid (1:1). Add 500 mL concentrated HCl to 400 mL Type II water. Dilute to 1 liter with Type II water.
- Standard stock solutions. May be purchased or prepared from ultrahigh purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hr at  $105^\circ\text{C}$ , unless otherwise specified.

**CAUTION:** Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

- Aluminum standard stock solution (100  $\mu\text{g}/\text{mL}$ ). Dissolve 0.1000 g of aluminum metal in an acid mixture of 4 mL of 1:1 HCl and 1 mL of concentrated  $\text{HNO}_3$  in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of 1:1 HCl. Dilute to 1 liter with Type II water.
- Calcium standard stock solution (100  $\mu\text{g}/\text{mL}$ ). Suspend 0.2500 g  $\text{CaCO}_3$  dried at  $180^\circ\text{C}$  for 1 hr before weighing in Type II water and dissolve cautiously with a minimum amount of 1:1  $\text{HNO}_3$ . Add 10.0 mL of concentrated  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
- Chromium standard stock solution (100  $\mu\text{g}/\text{mL}$ ). Dissolve 0.1900 g  $\text{CrO}_3$  in Type II water. When solution is complete, acidify with 10 mL concentrated  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
- Potassium standard stock solution (100  $\mu\text{g}/\text{mL}$ ). Dissolve 0.1900 g KCl dried at  $110^\circ\text{C}$  in Type II water. Dilute to 1 liter with Type II water.
- Sodium standard stock solution (100  $\mu\text{g}/\text{mL}$ ). Dissolve 0.2500 g NaCl in Type II water. Add 10.0 mL concentrated  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
- Nickel standard stock solution (100  $\mu\text{g}/\text{mL}$ ). Dissolve 0.1000 g of nickel metal in 10.0 mL hot concentrated  $\text{HNO}_3$ . Cool. Dilute to 1 liter with Type II water.
- Mixed calibration standard solutions. Care should be taken when preparing mixed standards for ICP analysis to ensure that the elements in the final mixed standard are compatible and stable together. One set of mixed calibration standards that has been found to be useful is listed in Table 3. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities.

To prepare the mixed calibration standard for chromium, combine appropriate volumes of the individual stock solutions indicated in Table 3 in volumetric flask. Add 2 mL 1:1  $\text{HNO}_3$  and 10 mL of 1:1 HCl and

dilute to 100 mL with Type II water. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see section 9.8) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Si
IV	Al, Ca, Cr, K, Na, and Ni

**NOTE:** Premixed standard solutions (traceable to NIST) containing the combined elements as listed in solutions I through IV are available from a number of commercial vendors.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Aqueous samples should be acidified to a pH of <2 with HNO<sub>3</sub>. A holding time of 6 months after sample collection is generally cited for this parameter.

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of aqueous samples to be analyzed for chromium.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Prepare a calibration blank (see section 9.4.1) and at least three mixed calibration standards in the appropriate concentration range to correlate chromium concentrations with the ICP's linear response range. Prepare standards for instrument calibration as instructed in section 5.14. Match the sample matrix and that of the standards as closely as possible.

Calibrate the instrument according to the instrument manufacturer's recommended procedures using typical mixed calibration standard solutions. Flush the system with the calibration blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

## 8.0 Procedure

1. Transfer a 100 mL representative aliquot of the well-mixed aqueous sample to a 150 mL Griffin beaker.
2. Add 3 mL of concentrated  $\text{HNO}_3$ . Cover the beaker with a ribbed watch glass.
3. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL) making certain that the sample does not boil and that no portion of the beaker is allowed to go dry.

**NOTE:** If a sample is allowed to go to dryness, low recoveries may result. Should this occur, repeat the steps 1 through 3 with a fresh sample aliquot.

4. Cool the beaker and add 3 mL of concentrated  $\text{HNO}_3$ .
5. Cover the beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.
6. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing).

7. Uncover the beaker, or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker.
8. Add a small quantity of 1:1 HCl (10 mL/100 of final solution) and warm the beaker for an additional 15 min to dissolve any precipitate or residue resulting from evaporation.
9. Wash down the beaker walls and watch glass with Type II water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer.

**NOTE:** Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and the filtering apparatus are thoroughly cleaned and prerinsed with dilute  $\text{HNO}_3$ .

10. Adjust to the final volume of 100 mL with Type II water. The sample is now ready for analysis.
11. The analyst should follow the instructions provided by the instrument's manufacturer. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range where coordination factors are valid. The analyst must: (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.
12. Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this conditions.
13. Flush the system with the calibration blank solution for at least 1 min before the analysis of each sample. Analyze samples.

**NOTE:** Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for chromium in aqueous solutions is 7 µg/L.

The method detection limit specified in this method is marginally sufficient to meet the Great Lakes Water Quality Criteria for chromium (16 µg/L). If concern is expressed for concentrations at or near the detection limit and Great Lakes Water Quality Criteria, a method for quantifying chromium using the graphite furnace atomic absorption procedure has been presented in this methods appendix.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured chromium concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance of the ICP and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be ± 15% of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Blanks

Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct

for possible contamination resulting from varying amounts of the acids used in the sample processing.

#### 9.4.1 Calibration Blank

The calibration blank is prepared by diluting 2 mL of 1:1 HNO<sub>3</sub> and of 1:1 HCl to 100 mL with Type II water. Prepare a sufficient quantity to flush the system between standards and samples.

The calibration blank should be analyzed prior to routine sample analysis, after every 10 samples, and at the end of the analytical run. The measured concentration in the calibration blank should be less than or equal to the method detection limit.

#### 9.4.2 Reagent Blank

The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

### 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

### 9.6 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - chromium, to the 100 mL aliquot of a routine sample for which an independent estimate of the target analyte

concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have a relative percent difference (RPD) of  $\leq 20\%$ .

### 9.7 Interference Check Sample

The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the method detection limit for each element. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

The interference check sample should be analyzed at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Results should be within  $\pm 20\%$  of the known concentration.

### 9.8 Calibration Control Sample

A calibration control sample should be prepared in the same acid matrix as the calibration standards at 10 times the method detection limit. This sample should be prepared in accordance with the instructions provided by the supplier. The calibration control sample is used to verify the integrity of the calibration standards on a weekly basis.

### 9.9 Recommended Tests

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

### 9.9.1 Serial Dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the method detection limit after dilution), an analysis of a 1:4 dilution should agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

### 9.9.2 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 10.0 Method Performance

In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was  $9 \pm 2\%$ . The mean percent recovery of spiked elements for all wastes was  $93 \pm 6\%$ . Spike levels ranged from 100  $\mu\text{g/L}$  to 100  $\text{mg/L}$ . The wastes included sludges and industrial wastewaters.

## 11.0 Calculations and Reporting

If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in  $\mu\text{g/L}$  with up to three significant figures.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Winge, R.K., V.J. Peterson, and V.A. Fassel. 1979. Inductively coupled plasma-atomic emission spectroscopy: Prominent lines, final report, March 1977 - February 1978, Ames laboratory, Ames, IA. EPA-600/4-79-017. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Table 1. Recommended Wavelengths and Estimated Instrumental Detection Limits.

Element	Wavelength <sup>a</sup> (nm)	Estimated Detection Limit <sup>b</sup> (µg/L)
Aluminum	308.215	45
Chromium	267.716	7
Copper	324.754	6
Nickel	231.604	15
Potassium	766.491	See footnote c
Sodium	588.995	29

a - The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see section 3.1).

b - The estimated instrumental detection limits are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

c - Highly dependent on operating conditions and plasma position.

Table 2. Analyte Concentration Equivalentents arising from Interference at the 100 mg/L Level.

Analyte	Wavelength (nm)	Interferant <sup>a,b</sup>									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Mo	Tl	V
Aluminum	308.215	-	-	-	-	-	-	0.21	-	-	1.4
Calcium	317.933	-	-	0.08	-	0.01	0.01	0.04	-	0.03	0.03
Chromium	267.716	-	-	-	-	0.003	-	0.04	-	-	0.04
Nickel	231.604	-	-	-	-	-	-	-	-	-	-
Sodium	588.995	0.30	-	-	-	-	-	-	-	-	-

a - Dashes indicate that no interference was observed even when interferants were introduced at the following levels:

Al - 1000 mg/L,  
 Ca - 1000 mg/L,  
 Cr - 200 mg/L,  
 Cu - 200 mg/L,  
 Fe - 1000 mg/L,  
 Mg - 1000 mg/L,  
 Mn - 200 mg/L,  
 Tl - 200 mg/L,  
 V - 200 mg/L, and

b - The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

Table 4. ICP Precision and Accuracy Data<sup>a</sup>

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)
Cr	150	149	3.8	10	10	18	50	50	3.3
Al	700	695	5.6	60	62	33	160	161	13
Ni	250	245	5.8	30	28	11	60	55	14

a - Not all elements were analyzed by all laboratories.

b - SD = standard deviation.

# CHROMIUM IN WATERS AND ELUTRIATES (GFAA)

## 1.0 Scope and Application

This method is an graphite furnace atomic absorption (GFAA) procedure suitable for the determination of chromium in natural water samples and mobility extracts such as sediment elutriates. All samples must be subjected to an acid digestion step prior to analysis.

This procedure is based on EPA SW-846 Methods 3020 for sample digestion and 7191 for chromium quantitation (USEPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

A mixture of nitric acid and the sample to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is cooled and brought up in dilute nitric acid such that the final dilution contains 3% (v/v) HNO<sub>3</sub>. If the sample contains suspended solids, it must be centrifuged, filtered, or allowed to settle.

Following sample digestion, a representative aliquot is slowly evaporated to dryness, charred (ashed), and atomized in a graphite furnace. The absorption of hollow cathode or EDL radiation during sample atomization is proportional to the chromium concentration.

## 3.0 Interferences

The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference, the serial dilution technique (see section 9.8.1) may be used. Those samples which indicate the presence of interference should be treated in one or more of the following ways:

1. Successively dilute and reanalyze the samples to eliminate interferences.
2. Modify the sample matrix either to remove interferences or to stabilize the analyte. Examples are the addition of ammonium nitrate to remove alkali chlorides and the addition of ammonium phosphate to retain cadmium. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.
3. Analyze the sample by method of standard additions while noticing the precautions and limitations of its use (see section 9.8.2).

Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, use either background correction or choose an alternate wavelength. Background correction may also compensate for nonspecific broad-band absorption interference.

Continuum background correction cannot correct for all types of background interference. When the background interference cannot be compensated for, chemically remove the analyte or use an alternate form of background correction, e.g., Zeeman background correction.

Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analyte.

Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Interference can also occur when resonant energy from another element in a multielement lamp, or from a metal impurity in the lamp cathode, falls within the bandpass of the slit setting when that other metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

Cross-contamination and contamination of the sample can be major sources of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in the Materials section (section 4.2). Pipet tips are

a frequent source of contamination. If other pipet tips are suspected of causing sample contamination, they should be acid soaked with 1:5 HNO<sub>3</sub> and rinsed thoroughly with tap and Type II water. The use of a better grade of pipet tip can greatly reduce this problem.

Pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five to ten high-temperature burns may be required to clean the tube before use.

Low concentrations of calcium and/or phosphate may cause interferences. At concentrations above 200 mg/L, calcium's effect is constant and eliminates the effect of phosphate. Calcium nitrate is therefore added to ensure a known constant effect.

Nitrogen should not be used as the purge gas because of a possible CN band interference.

Background correction may be required because nonspecific absorption and scattering can be significant at the analytical wavelength. Background correction with certain instruments may be difficult at this wavelength due to low-intensity output from hydrogen or deuterium lamps. Consult the specific instrument manufacturer's literature for details.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Electric hot plate, adjustable and capable of maintaining a temperature of 90-95° C.
4. Thermometer, 0 to 100° C range.
5. Atomic absorption spectrophotometer, single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip-chart recorder.

6. Chromium hollow cathode lamp, or electrodeless discharge lamp (EDL).
7. Graphite furnace. Any graphite furnace device with the appropriate temperature and timing controls.
8. Strip-chart recorder. A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, and changes in sensitivity can easily be recognized.

## 4.2 Materials

1. Commercial grade available argon and nitrogen are required for furnace work.
2. Griffin beakers, 150 mL, or equivalent.
3. Volumetric flasks, class A, 1 L.
4. Volumetric flasks, class A, 100 mL.
5. Pipets. Microliter with disposable tips. Sizes can range from 5 to 100  $\mu\text{L}$ , as required.

**NOTE:** All glassware, polypropylene, or Teflon containers, including sample bottles, should be washed in the following sequence: detergent, tap water, 1:1  $\text{HNO}_3$ , tap water, 1:1  $\text{HCl}$ , tap water, and Type II water.

**NOTE:** Chromic acid ( $\text{H}_2\text{CrO}_4$ ) should not be used as a cleaning agent for glassware if chromium is to be included in the analytical scheme for the sample digestate.

6. Watch glass, ribbed. Watch glass should be large enough to cover the mouth of the beaker.
7. Watch glass, non-ribbed. Watch glass should be large enough to cover the mouth of the beaker.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.

2. Calcium nitrate solution ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ). Dissolve 11.8 g of calcium nitrate,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (analytical reagent grade), in 500 mL of Type II water. Dilute to 1 liter with Type II water.
3. Concentrated hydrochloric acid (HCl), spectrograde grade certified for AA use. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid is <MDL, then the acid can be used.
4. Hydrochloric acid solution (HCl), 1:1. Add 500 mL of concentrated HCl to 400 mL of Type II water. Dilute to 1 liter with Type II water.
5. Concentrated nitric acid ( $\text{HNO}_3$ ), spectrograde grade certified for AA use. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid is <MDL, then the acid can be used.
6. Nitric acid solution ( $\text{HNO}_3$ ), 1:1. Add 500 mL of concentrated  $\text{HNO}_3$  to 400 mL of Type II water. Dilute to 1 liter with Type II water.
7. Chromium standard stock solution (1,000 mg/L). Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.923 g of chromium trioxide ( $\text{CrO}_3$ , analytical reagent grade) in Type II water. Acidify with 10 mL redistilled  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
8. Chromium working standards. Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. To each 100 mL of standard, add 1 mL of calcium nitrate solution. The calibration standard should be prepared to contain 0.5% (v/v)  $\text{HNO}_3$ .

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Water and elutriate samples should be acidified to a pH <2 with  $\text{HNO}_3$ . A holding time of 6 months is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water (see note in section 4.2). Either glass or plastic containers can be used for the storage of samples to be analyzed for chromium in aqueous samples.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^\circ \text{C}$ .

The hot plate should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^\circ \text{C}$ .

Prepare a method blank and at least three standards in the appropriate concentration range to correlate chromium concentrations with the atomic absorption spectrophotometer's linear response range. Prepare standards for instrument calibration by appropriate dilution of the chromium standard stock solution. These standards should be prepared fresh on the day of use. Match the sample matrix and that of the standards as closely as possible.

Inject a suitable portion of each standard into the graphite furnace in order of increasing concentration. It is recommended that each standard solution be analyzed in triplicate in order to assess method precision. Instrument calibration curves should be composed of a minimum of a blank and three standards. A calibration curve should be prepared every day of continuous sample analysis and prior to the initiation of the project's routine sample analysis.

Construct an analytical curve by plotting the average peak absorbance or peak area for the standard solutions as a function of sample concentration on a linear graph. Prepare this graph daily when new initial calibration information is obtained. Alternatively, electronic instrument calibration can be used if the instrument is appropriately equipped.

## 8.0 Procedure

### 8.1 Sample Preparation

1. Transfer 100 mL of well mixed sample to a 150 mL Griffin beaker.
2. Add 3 mL of concentrated  $\text{HNO}_3$ .
3. Cover the beaker with a ribbed watch glass.

4. Place the beaker on a hot plate and cautiously evaporate to a low volume (approximately 5 mL) making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry.
5. Cool the digested sample and add 3 mL of concentrated HNO<sub>3</sub>.
6. Cover the beaker with a non-ribbed watch glass.
7. Place the beaker on a hot plate and increase the temperature so that a gentle reflux action occurs.
8. Continue heating, adding additional acid as necessary, until the digestion is complete.

**NOTE:** Complete digestion is generally indicated by a light digestate color or if the digestate does not change in appearance with continued refluxing.

9. When the digestion is complete, cover with a ribbed watch glass and evaporate to a low volume (approximately 3 mL).

**NOTE:** Do not allow any portion of the beaker bottom to go dry.

10. Add approximately 10 mL of Type II water and mix.
11. Continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.
12. Remove beaker from hot plate and wash down the beaker walls and watch glass with Type II water.

**NOTE:** It may be necessary to filter or centrifuge the sample to remove silicates and other insoluble material that may interfere with injecting the sample into the graphite furnace.

13. Adjust the final volume to 100 mL with Type II water.
14. Add 1 mL of calcium nitrate solution to each sample. The sample is now ready for analysis.

## 8.2 Sample Analysis

1. The 357.9 nm wavelength line and a background correction system are required. Follow the manufacturer's suggestions for all other spectrophotometer parameters.
2. Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing

mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

3. Inject a measured microliter ( $\mu\text{L}$ ) aliquot of sample digest into the furnace and atomize. If the digest concentration is greater than the highest standard, or if the instrument response falls on the plateau of the calibration curve, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for chromium in waters and elutriates is 1  $\mu\text{g/L}$ .

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured chromium concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standard 1643c - Water, should be run to monitor the life and performance of the graphite tube and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

## 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a water sample, prepared by spiking ASTM Type II water at the laboratory, and that has undergone multiple analyses by the analytical laboratory. The lot numbers of the As stock solution used in the creation of the LCS should be different from those used to prepare the calibration (both initial and ongoing) standards. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

## 9.5 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 15 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.7 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - chromium, to the 100 mL sample aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 3 times the estimated or actual method detection limit. The added matrix spike should have a negligible volume when compared to the routine sample volume to eliminate/control sample dilution effects. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 20\%$ .

## 9.8 Recommended Tests

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values. Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition may be used (see Section 9.8.2).

### 9.8.1 Serial Dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the method detection limit after dilution), an analysis of a 1:4 dilution should agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

### 9.8.2 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through

the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 10.0 Method Performance

The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-100  $\mu\text{g/L}$ .  
Detection limit: 1  $\mu\text{g/L}$ .

Precision and accuracy data shown in Table 1 were obtained from records of state and contractor laboratories (USEPA, 1979).

## 11.0 Calculations and Reporting

Calculate metal concentrations by (1) the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account.

The method of standard additions is the preferred method for the analysis of all sediment elutriates to compensate for any sample matrix effects.

Prepare a standard curve based on the absorbance and concentration of the chromium standards. Determine the chromium concentration in each of the

sample digests by comparing the digest absorbance with the standard calibration curve.

If dilution of sample was required, the following formula is provided to account for the dilution:

$$\text{Cr, } \mu\text{g/L} = \frac{A \times (B + C)}{C}$$

where:

A = metal in diluted aliquot from calibration curve,  $\mu\text{g/L}$ .

B = acid blank matrix used for dilution, mL.

C = sample aliquot, mL.

Chromium concentrations in water or elutriate samples should be reported in  $\mu\text{g/L}$ .

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. 17th Edition, APHA, New York, New York.

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Table 1. Method Performance Data.

Number of Labs	True Value µg/L	Mean Value µg/L	Standard Deviation µg/L	Accuracy as % Bias
74	370	353	105	-4.5
76	407	380	128	-6.5
72	74	72	29	-3.1
70	93	84	35	-10.2
47	7.4	10.2	7.8	37.7
47	15.0	16.0	9.0	6.8

# COPPER IN WATERS AND ELUTRIATES (ICP)

## 1.0 Scope and Application

Inductively coupled plasma atomic emission spectroscopy (ICP) determines copper and numerous other elements that are present in aqueous samples, such as surface water and elutriate samples. The aqueous samples must first be digested with nitric acid prior to analysis.

Detection limits, sensitivity, and optimum concentration ranges for copper, and other metals stable in a mixed standard solution with copper, will vary with the sample aliquot size, the spectrophotometer being used, and possible matrix interferences. The data shown in Table 1 provide concentration ranges for clean aqueous samples.

The method of standard addition (MSA) shall be used for the analysis of all sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required (see section 9).

This method should only be used by spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

This procedure is based on SW-846 Methods 3010 (for digestion) and 6010 for quantitation (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

Prior to analysis, the samples to be analyzed are refluxed with nitric acid in a covered beaker. This step is repeated with additional HNO<sub>3</sub> until the final digestate is light in color and diluted to volume.

This instrumental method measures light emitted by copper in the final digest by optical spectrometry. The digested samples are nebulized and the resulting aerosol is transported to a plasma torch. Copper-specific atomic-line emission

spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes.

Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

The possibility of additional interferences named in section 3.0 should also be recognized and appropriate corrections made when necessary. The procedures that can be used for this purpose are described in section 9.

### 3.0 Interferences

There are three main forms of interferences that can occur during the analysis of water and elutriate samples by ICP. These three types of interferences include: (1) spectral, (2) physical, and (3) chemical interferences. Each is discussed separately in the following sections.

#### 3.1 Spectral Interferences

Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multi-element instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended

as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferants can be assumed.

The magnitude of the interference effects summarized in Table 2 are expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that Cu is to be determined (at 324.754 nm) in a sample containing approximately 10 mg/L of V. According to Table 2, 100 mg/L of V would yield a false signal for Cu equivalent to approximately 0.02 mg/L. Therefore, the presence of 10 mg/L of V would result in a false signal for Cu equivalent to approximately 0.002 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, and argon flow rate.

The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

### 3.2 Physical Interferences

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Further, it has been reported that better control of the argon flow rate improves instrument performance. Improved argon flow rate control can be accomplished with the use of mass flow controllers.

### 3.3 Chemical Interferences

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant

with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, etc.), buffering of the sample, matrix matching, and standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Centrifuge and centrifuge tubes.
4. Electric hot plate, adjustable and capable of maintaining a temperature of 90-95° C.
5. Inductively coupled argon plasma emission spectrometer.
6. Computer-controlled emission spectrometer with background correction.
7. Radio frequency generator.
8. Argon gas supply, welding grade or better.

### 4.2 Materials

1. Griffin beakers, 150 mL, or equivalent.
2. Watch glasses, ribbed and plain.
3. Whatman No. 41 filter paper, or equivalent.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
3. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.

- Nitric acid (1:1). Add 500 mL concentrated  $\text{HNO}_3$  to 400 mL Type II water. Dilute to 1 liter with Type II water.
- Hydrochloric acid (1:1). Add 500 mL concentrated  $\text{HCl}$  to 400 mL Type II water. Dilute to 1 liter with Type II water.
- Standard stock solutions. May be purchased or prepared from ultrahigh purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hr at  $105^\circ\text{C}$ , unless otherwise specified.

**CAUTION:** Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

- Barium standard stock solution ( $100\ \mu\text{g/mL}$ ). Dissolve 0.1500 g  $\text{BaCl}_2$  dried at  $250^\circ\text{C}$  for 2 hr in 10 mL Type II water with 1 mL 1:1  $\text{HCl}$ . Add 10.0 mL 1:1  $\text{HCl}$ . Dilute to 1 liter with Type II water.
- Cobalt standard stock solution ( $100\ \mu\text{g/mL}$ ). Dissolve 0.1000 g of cobalt metal in a minimum amount of 1:1  $\text{HNO}_3$ . Add 10.0 mL 1:1  $\text{HCl}$ . Dilute to 1 liter with Type II water.
- Copper standard stock solution ( $100\ \mu\text{g/mL}$ ). Dissolve 0.1300 g  $\text{CuO}$  in a minimum amount of 1:1  $\text{HNO}_3$ . Add 10.0 mL concentrated  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
- Iron standard stock solution ( $100\ \mu\text{g/mL}$ ). Dissolve 0.1400 g  $\text{Fe}_2\text{O}_3$  in a warm mixture of 20 mL 1:1  $\text{HCl}$  and 2 mL of concentrated  $\text{HNO}_3$ . Cool. Add an additional 5.0 mL of concentrated  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
- Vanadium standard stock solution ( $100\ \mu\text{g/mL}$ ). Dissolve 0.2300 g  $\text{NH}_4\text{VO}_3$  in a minimum amount of concentrated  $\text{HNO}_3$ . Heat to increase rate of dissolution. Add 10.0 mL concentrated  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
- Mixed calibration standard solutions. Care should be taken when preparing mixed standards for ICP analysis to ensure that the elements in the final mixed standard are compatible and stable together. One set of mixed calibration standards that has been found to be useful is listed in Table 3. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities.

To prepare the mixed calibration standard for copper, combine appropriate volumes of the individual stock solutions indicated in Table 3 in volumetric flask. Add 2 mL 1:1  $\text{HNO}_3$  and 10 mL of 1:1  $\text{HCl}$  and dilute to 100 mL with Type II water. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be

prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see section 9.8) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Si
IV	Al, Ca, Cr, K, Na, and Ni

**NOTE:** Premixed standard solutions (traceable to NIST) containing the combined elements as listed in solutions I through IV are available from a number of commercial vendors.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Aqueous samples should be acidified to a pH of <2 with HNO<sub>3</sub>. A holding time of 6 months after sample collection is generally cited for this parameter.

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of aqueous samples to be analyzed for copper.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Prepare a calibration blank (see section 9.4.1) and at least three mixed calibration standards in the appropriate concentration range to correlate copper concentrations with the ICP's linear response range. Prepare standards for instrument calibration as instructed in section 5.13. Match the sample matrix and that of the standards as closely as possible.

Calibrate the instrument according to the instrument manufacturer's recommended procedures using typical mixed calibration standard solutions. Flush the system with the calibration blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

## 8.0 Procedure

1. Transfer a 100 mL representative aliquot of the well-mixed aqueous sample to a 150 mL Griffin beaker.
2. Add 3 mL of concentrated  $\text{HNO}_3$ . Cover the beaker with a ribbed watch glass.
3. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL) making certain that the sample does not boil and that no portion of the beaker is allowed to go dry.

**NOTE:** If a sample is allowed to go to dryness, low recoveries may result. Should this occur, repeat the steps 1 through 3 with a fresh sample aliquot.

4. Cool the beaker and add 3 mL of concentrated  $\text{HNO}_3$ .
5. Cover the beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.
6. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing).

7. Uncover the beaker, or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker.
8. Add a small quantity of 1:1 HCl (10 mL/100 of final solution) and warm the beaker for an additional 15 min to dissolve any precipitate or residue resulting from evaporation.
9. Wash down the beaker walls and watch glass with Type II water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer.

**NOTE:** Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and the filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO<sub>3</sub>.

10. Adjust to the final volume of 100 mL with Type II water. The sample is now ready for analysis.
11. The analyst should follow the instructions provided by the instrument's manufacturer. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range where coordination factors are valid. The analyst must: (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.
12. Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this conditions.
13. Flush the system with the calibration blank solution for at least 1 min before the analysis of each sample. Analyze samples.

**NOTE:** Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for copper in aqueous solutions is 6 µg/L.

The method detection limit specified in this method is insufficient to meet the Great Lakes Water Quality Criteria for copper (7.3 µg/L). However, this method has been presented to allow for the use of the ICP as a screening tool for copper. If the measured concentrations are greater than 7.3 µg/L, the Great Lakes Water Quality Criteria has been violated and no further analyses are needed. However, if the measured concentration is below 7.3 µg/L, copper must be quantified using the graphite furnace atomic absorption procedure presented in this appendix.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured copper concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance of the ICP and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be ± 15% of the known value or within the certified value provided by the supplier, whichever is larger.

## 9.4 Blanks

Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

### 9.4.1 Calibration Blank

The calibration blank is prepared by diluting 2 mL of 1:1 HNO<sub>3</sub> and of 1:1 HCl to 100 mL with Type II water. Prepare a sufficient quantity to flush the system between standards and samples.

The calibration blank should be analyzed prior to routine sample analysis, after every 10 samples, and at the end of the analytical run. The measured concentration in the calibration blank should be less than or equal to the method detection limit.

### 9.4.2 Reagent Blank

The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.6 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - copper, to the 100 mL aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have a relative percent difference (RPD) of  $\leq 20\%$ .

## 9.7 Interference Check Sample

The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the method detection limit for each element. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

The interference check sample should be analyzed at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Results should be within  $\pm 20\%$  of the known concentration.

## 9.8 Calibration Control Sample

A calibration control sample should be prepared in the same acid matrix as the calibration standards at 10 times the method detection limit. This sample should be prepared in accordance with the instructions provided by the supplier. The calibration control sample is used to verify the integrity of the calibration standards on a weekly basis.

## 9.9 Recommended Tests

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests will ensure the analyst that neither positive nor

negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

### 9.9.1 Serial Dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the method detection limit after dilution), an analysis of a 1:4 dilution should agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

### 9.9.2 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 10.0 Method Performance

In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was  $9 \pm 2\%$ . The mean percent recovery of spiked elements for all wastes was  $93 \pm 6\%$ . Spike levels ranged from 100  $\mu\text{g/L}$  to 100  $\text{mg/L}$ . The wastes included sludges and industrial wastewaters.

## 11.0 Calculations and Reporting

If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in  $\mu\text{g/L}$  with up to three significant figures.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Winge, R.K., V.J. Peterson, and V.A. Fassel. 1979. Inductively coupled plasma-atomic emission spectroscopy: Prominent lines, final report, March 1977 - February 1978, Ames laboratory, Ames, IA. EPA-600/4-79-017. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Table 1. Recommended Wavelengths and Estimated Instrumental Detection Limits.

Element	Wavelength <sup>a</sup> (nm)	Estimated Detection Limit <sup>b</sup> (µg/L)
Barium	455.403	2
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Vanadium	292.402	8

a - The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see section 3.1).

b - The estimated instrumental detection limits are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

Table 2. Analyte Concentration Equivalents arising from Interference at the 100 mg/L Level.

Analyte	Wavelength (nm)	Interferant <sup>a,b</sup>									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Mo	Tl	V
Barium	455.403	-	-	-	-	-	-	-	-	-	-
Cobalt	228.616	-	-	0.03	-	0.005	-	-	0.03	0.15	-
Copper	324.754	-	-	-	-	0.003	-	-	-	0.05	0.02
Iron	259.940	-	-	-	-	-	-	0.12	-	-	-
Vanadium	292.402	-	-	0.05	-	0.005	-	-	-	0.02	-

a - Dashes indicate that no interference was observed even when interferants were introduced at the following levels:

Al - 1000 mg/L,  
 Ca - 1000 mg/L,  
 Cr - 200 mg/L,  
 Cu - 200 mg/L,  
 Fe - 1000 mg/L,  
 Mg - 1000 mg/L,  
 Mn - 200 mg/L,  
 Tl - 200 mg/L,  
 V - 200 mg/L, and

b - The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

Table 4. ICP Precision and Accuracy Data<sup>a</sup>

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)
V	750	749	1.8	70	69	2.9	170	169	1.1
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Co	700	512	10	20	20	4.1	120	108	21

a - Not all elements were analyzed by all laboratories.

b - SD = standard deviation.

# COPPER IN WATERS AND ELUTRIATES (GFAA)

## 1.0 Scope and Application

This method is an graphite furnace atomic absorption (GFAA) procedure suitable for the determination of copper in natural water samples and mobility extracts such as sediment elutriates. All samples must be subjected to an acid digestion step prior to analysis.

This procedure is based on EPA SW-846 Methods 3020 for sample digestion and 7211 for copper quantitation (USEPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

A mixture of nitric acid and the sample to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is cooled and brought up in dilute nitric acid such that the final dilution contains 3% (v/v) HNO<sub>3</sub>. If the sample contains suspended solids, it must be centrifuged, filtered, or allowed to settle.

Following sample digestion, a representative aliquot is slowly evaporated to dryness, charred (ashed), and atomized in a graphite furnace. The absorption of hollow cathode or EDL radiation during sample atomization is proportional to the copper concentration.

## 3.0 Interferences

The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference, the serial dilution technique (see section 9.8.1) may be used. Those samples which indicate the presence of interference should be treated in one or more of the following ways:

1. Successively dilute and reanalyze the samples to eliminate interferences.
2. Modify the sample matrix either to remove interferences or to stabilize the analyte. Examples are the addition of ammonium nitrate to remove alkali chlorides and the addition of ammonium phosphate to retain cadmium. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.
3. Analyze the sample by method of standard additions while noticing the precautions and limitations of its use (see section 9.8.2).

Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, use either background correction or choose an alternate wavelength. Background correction may also compensate for nonspecific broad-band absorption interference.

Continuum background correction cannot correct for all types of background interference. When the background interference cannot be compensated for, chemically remove the analyte or use an alternate form of background correction, e.g., Zeeman background correction.

Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analyte.

Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Interference can also occur when resonant energy from another element in a multielement lamp, or from a metal impurity in the lamp cathode, falls within the bandpass of the slit setting when that other metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

Cross-contamination and contamination of the sample can be major sources of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in the Materials section (section 4.2). Pipet tips are

a frequent source of contamination. If other pipet tips are suspected of causing sample contamination, they should be acid soaked with 1:5 HNO<sub>3</sub> and rinsed thoroughly with tap and Type II water. The use of a better grade of pipet tip can greatly reduce this problem.

Pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five to ten high-temperature burns may be required to clean the tube before use.

Background correction may be required because nonspecific absorption and scattering can be significant at the analytical wavelength. Background correction with certain instruments may be difficult at this wavelength due to low-intensity output from hydrogen or deuterium lamps. Consult the specific instrument manufacturer's literature for details.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Electric hot plate, adjustable and capable of maintaining a temperature of 90-95° C.
4. Thermometer, 0 to 100° C range.
5. Atomic absorption spectrophotometer, single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip-chart recorder.
6. Copper hollow cathode lamp, or electrodeless discharge lamp (EDL).
7. Graphite furnace. Any graphite furnace device with the appropriate temperature and timing controls.
8. Strip-chart recorder. A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, and changes in sensitivity can easily be recognized.

## 4.2 Materials

1. Commercial grade available argon and nitrogen are required for furnace work.
2. Griffin beakers, 150 mL, or equivalent.
3. Volumetric flasks, class A, 1 L.
4. Volumetric flasks, class A, 100 mL.
5. Pipets. Microliter with disposable tips. Sizes can range from 5 to 100  $\mu\text{L}$ , as required.

**NOTE:** All glassware, polypropylene, or Teflon containers, including sample bottles, should be washed in the following sequence: detergent, tap water, 1:1  $\text{HNO}_3$ , tap water, 1:1  $\text{HCl}$ , tap water, and Type II water.

**NOTE:** Chromic acid ( $\text{H}_2\text{CrO}_4$ ) should not be used as a cleaning agent for glassware if chromium is to be included in the analytical scheme for the sample digestate.

6. Watch glass, ribbed. Watch glass should be large enough to cover the mouth of the beaker.
7. Watch glass, non-ribbed. Watch glass should be large enough to cover the mouth of the beaker.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
3. Concentrated hydrochloric acid ( $\text{HCl}$ ), spectrograde grade certified for AA use. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid is  $<\text{MDL}$ , then the acid can be used.
4. Hydrochloric acid solution ( $\text{HCl}$ ), 1:1. Add 500 mL of concentrated  $\text{HCl}$  to 400 mL of Type II water. Dilute to 1 liter with Type II water.
5. Concentrated nitric acid ( $\text{HNO}_3$ ), spectrograde grade certified for AA use. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid is  $<\text{MDL}$ , then the acid can be used.

6. Nitric acid solution ( $\text{HNO}_3$ ), 1:1. Add 500 mL of concentrated  $\text{HNO}_3$  to 400 mL of Type II water. Dilute to 1 liter with Type II water.
7. Copper standard stock solution (1,000 mg/L). Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.00 g of electrolytic copper, analytical reagent grade) in 5 mL of re-distilled  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
8. Copper working standards. Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. The calibration standard should be prepared to contain 0.5% (v/v)  $\text{HNO}_3$ .

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Water and elutriate samples should be acidified to a pH <2 with  $\text{HNO}_3$ . A holding time of 6 months is generally cited for this parameter.

Samples should be stored under refrigerated conditions ( $4^\circ \text{C}$ ).

All sample containers must be prewashed with detergents, acids, and Type II water (see note in section 4.2). Either glass or plastic containers can be used for the storage of samples to be analyzed for copper in aqueous samples.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^\circ \text{C}$ .

The hot plate should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^\circ \text{C}$ .

Prepare a method blank and at least three standards in the appropriate concentration range to correlate copper concentrations with the atomic absorption spectrophotometer's linear response range. Prepare standards for instrument calibration by appropriate dilution of the copper standard stock solution. These standards should be prepared fresh on the day of use. Match the sample matrix and that of the standards as closely as possible.

Inject a suitable portion of each standard into the graphite furnace in order of increasing concentration. It is recommended that each standard solution be analyzed in triplicate in order to assess method precision. Instrument calibration curves should be composed of a minimum of a blank and three standards. A calibration curve should be prepared every day of continuous sample analysis and prior to the initiation of the project's routine sample analysis.

Construct an analytical curve by plotting the average peak absorbance or peak area for the standard solutions as a function of sample concentration on a linear graph. Prepare this graph daily when new initial calibration information is obtained. Alternatively, electronic instrument calibration can be used if the instrument is appropriately equipped.

## 8.0 Procedure

### 8.1 Sample Preparation

1. Transfer 100 mL of well mixed sample to a 150 mL Griffin beaker.
2. Add 3 mL of concentrated HNO<sub>3</sub>.
3. Cover the beaker with a ribbed watch glass.
4. Place the beaker on a hot plate and cautiously evaporate to a low volume (approximately 5 mL) making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry.
5. Cool the digested sample and add 3 mL of concentrated HNO<sub>3</sub>.
6. Cover the beaker with a non-ribbed watch glass.
7. Place the beaker on a hot plate and increase the temperature so that a gentle reflux action occurs.
8. Continue heating, adding additional acid as necessary, until the digestion is complete.

**NOTE:** Complete digestion is generally indicated by a light digestate color or if the digestate does not change in appearance with continued refluxing.

9. When the digestion is complete, cover with a ribbed watch glass and evaporate to a low volume (approximately 3 mL).

**NOTE:** Do not allow any portion of the beaker bottom to go dry.

10. Add approximately 10 mL of Type II water and mix.
11. Continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.
12. Remove beaker from hot plate and wash down the beaker walls and watch glass with Type II water.

**NOTE:** It may be necessary to filter or centrifuge the sample to remove silicates and other insoluble material that may interfere with injecting the sample into the graphite furnace.

13. Adjust the final volume to 100 mL with Type II water.

## 8.2 Sample Analysis

1. The 324.7 nm wavelength line and a background correction system are required. Follow the manufacturer's suggestions for all other spectrophotometer parameters.
2. Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.
3. Inject a measured microliter ( $\mu\text{L}$ ) aliquot of sample digest into the furnace and atomize. If the digest concentration is greater than the highest standard, or if the instrument response falls on the plateau of the calibration curve, the sample should be diluted in the same

acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for copper in waters and elutriates is 1 µg/L.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured copper concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standard 1643c - Water, should be run to monitor the life and performance of the graphite tube and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a water sample, prepared by spiking ASTM Type II water at the laboratory, and that has undergone multiple analyses by the analytical laboratory. The lot numbers of the As stock solution used in the creation of the LCS should be different from those used to prepare the calibration (both initial and ongoing) standards. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

## 9.5 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 15 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.7 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - copper, to the 100 mL sample aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 3 times the estimated or actual method detection limit. The added matrix spike should have a negligible volume when compared to the routine sample volume to eliminate/control sample dilution effects. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 20\%$ .

## 9.8 Recommended Tests

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values. Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition may be use (see Section 9.8.2).

### 9.8.1 Serial Dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the method detection limit after dilution), an analysis of a 1:4 dilution should agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

### 9.8.2 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 10.0 Method Performance

The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-100 µg/L.

Detection limit: 1 µg/L.

Precision and accuracy data shown in Table 1 were obtained from records of state and contractor laboratories (USEPA, 1979).

## 11.0 Calculations and Reporting

Calculate metal concentrations by (1) the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account.

The method of standard additions is the preferred method for the analysis of all sediment elutriates to compensate for any sample matrix effects.

Prepare a standard curve based on the absorbance and concentration of the copper standards. Determine the copper concentration in each of the sample digests by comparing the digest absorbance with the standard calibration curve.

If dilution of sample was required, the following formula is provided to account for the dilution:

$$\text{Cu, } \mu\text{g/L} = \frac{A \times (B + C)}{C}$$

where:

A = metal in diluted aliquot from calibration curve, µg/L.

B = acid blank matrix used for dilution, mL.

C = sample aliquot, mL.

Copper concentrations in water or elutriate samples should be reported in  $\mu\text{g/L}$ .

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. 17th Edition, APHA, New York, New York.

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Table 1. Method Performance Data.

Number of Labs	True Value $\mu\text{g/L}$	Mean Value $\mu\text{g/L}$	Standard Deviation $\mu\text{g/L}$	Accuracy as % Bias
91	302	305	56	0.9
92	332	324	56	-2.4
86	60	64	23	7.0
84	75	76	22	1.3
66	7.5	9.7	6.1	29.7
66	12.0	13.9	9.7	15.5

# MERCURY IN WATER AND ELUTRIATES (MANUAL CVAA)

## 1.0 Scope and Application

This method is applicable to the determination of mercury in liquid samples, such as surface waters and sediment elutriates. All samples must be subjected to an appropriate dissolution step prior to analysis.

In addition to the inorganic forms, mercury may also be present as an organic compound. Although potassium permanganate oxidizes many of these compounds, recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. However, the use of potassium persulfate as an oxidant has been found to produce approximately 100% recovery of these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be converted to the mercuric ion prior to sample analysis. In order to ensure conversion of methyl mercuric chloride, it is necessary to heat the samples during the pretreatment procedure.

This procedure is based on SW-846 Method 7470 (USEPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

Mercury in a sample aliquot is treated with an oxidant to reduce it to the elemental state. The sample is attached to a cold vapor atomic absorption apparatus and the elemental mercury is flushed from the sample in a stream of air. The mercury vapor is passed through a cell positioned in the light path of an atomic absorption spectrophotometer. The mercury concentration in the sample is proportional to the absorption (peak height) of incident radiation with a wavelength of 253.7 nm.

## 3.0 Interferences

Potassium permanganate is added during the sample preparation step to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from ASTM Type II water.

Although copper has also been reported to interfere with the analysis of mercury, studies suggest that copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

Interference from certain volatile organic materials, which may absorb radiation at a wavelength of 253 nm, is also possible but seldom encountered (USEPA, 1979). A preliminary run without reagents can be performed to identify the presence of and to correct for this matrix effect.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, 3-5 weights covering expected weight range.
3. Electric hot plate, adjustable and capable of maintaining a temperature of 90-95° C.
4. Thermometer, 0 to 100° C range.
5. Atomic absorption spectrophotometer. Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.
6. Mercury hollow cathode lamp or electrodeless discharge lamp.
7. Recorder. Any multi-range variable-speed recorder that is compatible with the UV detection system is suitable.
8. Absorption cell. Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 2.54 cm O.D. x 11.43 cm. The ends are ground perpendicular to the longitudinal axis, and quartz windows (2.54 cm diameter x 0.16 cm thickness) are

cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 5.08 cm x 5.08 cm cards. Holes with a diameter of 2.54 cm are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

9. Air pump. Any peristaltic pump capable of delivering 1 L/min air may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.
10. Flowmeter. Capable of measuring an air flow of 1 L/min.
11. Aeration tube. A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.
12. Drying tube, 15.2 cm X 1.90 cm diameter tube containing 20 g of magnesium perchlorate.

**NOTE:** In place of the magnesium perchlorate drying tube, a small reading lamp with a 60 W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10° C above ambient.

13. Cold vapor generator.
  - a. The apparatus shown in Figure 1 is a closed system. An open system, in which the mercury vapor is passed through the absorption cell only once, may be used in place of the closed system.
  - b. Because mercury vapor is potentially toxic, precautions must be taken to avoid inhalation of the vapor. Therefore, a bypass has been included in the analytical apparatus to either vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium such as:
    1. equal volumes of 0.1 M  $\text{KMnO}_4$  and 10%  $\text{H}_2\text{SO}_4$ ,
    2. 0.25% iodine in a 3% KI solution, or
    3. specially treated charcoal that will absorb mercury vapor.

## 4.2 Materials

1. BOD bottles, 300 mL, or equivalent.
2. Volumetric flasks, class A, 100 mL.
3. Graduated cylinders, various sizes up to 100 mL, or equivalent.

## 5.0 Reagents and Standards

1. ASTM Type II water (ASTM D1193). Water supply should be continually tested to verify that contaminants are not present at levels that will interfere with method performance.
2. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), conc. reagent grade.
3. Sulfuric acid, 0.5 N. Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter with ASTM Type II water.
4. Nitric acid ( $\text{HNO}_3$ ), conc. reagent grade with low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.
5. Stannous sulfate. Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use.

**NOTE:** Stannous chloride may be used in place of stannous sulfate.

6. Sodium chloride-hydroxylamine sulfate solution. Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in ASTM Type II water. Dilute to 100 mL with Type II water.

**NOTE:** Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

7. Potassium permanganate, 5% w/v solution ( $\text{KMnO}_4$ ). Dissolve 5 g of potassium permanganate in 100 mL of ASTM Type II water.
8. Potassium Persulfate, 5% w/v solution. Dissolve 5 g of potassium persulfate in 100 mL of ASTM Type II water.
9. Mercury stock solution. Dissolve 0.1354 g of mercuric chloride in 75 mL of ASTM Type II water. Add 10 mL of concentrated nitric acid and adjust the volume to 100 mL with ASTM Type II water. (1.0 mL = 1.0 mg Hg).
10. Mercury working solution. Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1  $\mu\text{g}/\text{mL}$ . This working standard and the dilution of the stock mercury solutions

should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding mercury stock solution.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Water and elutriate samples should be acidified to a pH <2 with HNO<sub>3</sub>. A holding time of 28 days is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of samples to be analyzed for arsenic in sediments.

If only dissolved mercury is to be determined, the sample should be filtered through an all glass apparatus before the acid is added. If total mercury is to be determined, the filtration is omitted.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^{\circ}$  C.

The hot plate/water bath should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^{\circ}$  C.

Calibration curves should be composed of a minimum of a blank and three standards. To calibrate and standardize to atomic absorption

spectrophotometer, the following steps should be used to prepare standards and prepare the instrument:

1. Transfer 0.0, 0.5, 1.0, 2.0, 5.0, and 10-mL aliquots of the mercury working standard containing 0-1.0  $\mu\text{g}$ , respectively, of mercury to a series of 300-mL BOD bottles.
2. Add enough ASTM Type II water to each bottle to make a total volume of 100 mL.
3. Mix thoroughly and add 5 mL of conc. sulfuric acid and 2.5 mL of conc. nitric acid to each bottle.
4. Add 15 mL of  $\text{KMnO}_4$  solution to each bottle and allow to stand at least 15 minutes.
5. Add 8 mL of potassium persulfate to each bottle and heat for 2 hours in a water bath maintained at  $95^\circ\text{C}$ .
6. Allow the standards to cool.
7. Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate.
8. When the solution has been decolorized, wait 30 seconds, add 5 mL of stannous sulfate solution, and immediately attach the bottle to the aeration apparatus. At this point, the sample is allowed to stand quietly without manual agitation.
9. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to a minimum value. Due to the potential toxicity of these vapors, they should be properly vented through a fume hood or absorbing medium.
10. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue the aeration.
11. Repeat steps 6 through 10 for each of the standards.
12. Construct a standard curve by plotting the recorded absorbance versus the concentration of mercury in the standards.

## 8.0 Procedure

1. Transfer 100 mL of sample, or a suitable size aliquot diluted to 100 mL, containing not more than 1.0  $\mu\text{g}$  of mercury, to a 300 mL BOD bottle.

2. Add 5 mL of conc. sulfuric acid and 2.5 mL of conc. nitric acid mixing after each addition.
3. Add 15 mL of potassium permanganate solution to each sample bottle and shake. If necessary, add additional potassium permanganate until the purple color persists for at least 15 minutes.
4. Add 8 mL of potassium persulfate to each bottle and heat for 2 hours in a water bath at 95° C.
5. Allow the samples to cool.
6. To the first sample, add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.
7. After a delay of at least 30 seconds, add 5 mL of stannous sulfate solution, and immediately attach the bottle to the aeration apparatus. At this point, the sample is allowed to stand quietly without manual agitation.
8. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to a minimum value. Due to the potential toxicity of these vapors, they should be properly vented through a fume hood or absorbing medium.
9. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue the aeration.
10. Repeat steps 6 through 9 for each of the samples.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for mercury in waters and elutriates is 0.2 µg/L.

## 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured arsenic concentrations.

## 9.3 Standard Reference Materials

Standard reference materials, such as NIST standard 1643c - Water, should be run to monitor the life and performance of the graphite tube and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

## 9.4 Laboratory Control Samples

A laboratory control sample (LCS) should be developed and maintained by the analytical laboratory. A laboratory control sample is a water sample, prepared by spiking ASTM Type II water at the laboratory, and that has undergone multiple analyses by the analytical laboratory. The lot numbers of the As stock solution used in the creation of the LCS should be different from those used to prepare the calibration (both initial and ongoing) standards. The measured concentration of the laboratory control sample should be within  $\pm 3$  standard deviation units from the mean concentration of the LCS.

## 9.5 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the instrument detection limit.

## 9.6 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 15 samples. The ongoing calibration check sample should be a mid-calibration range standard

prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.7 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - arsenic, to the 100 mL sample aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 3 times the estimated or actual method detection limit. The added matrix spike should have a negligible volume when compared to the routine sample volume to eliminate/control sample dilution effects. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 20\%$ .

## 10.0 Method Performance

The working range of this method is 0.2  $\mu\text{g/L}$  to 20  $\mu\text{g/L}$  although the actual range can be modified through instrument and/or recorder expansion.

In a single laboratory (EMSL-Cincinnati), using an Ohio River composite sample with a background mercury concentration of 0.35  $\mu\text{g/L}$ , spiked with concentrations of 1.0, 3.0 and 4.0  $\mu\text{g/L}$ , the standard deviations were  $\pm 0.14$ ,  $\pm 0.10$  and  $\pm 0.08$ , respectively. The standard deviation at the 0.35  $\mu\text{g/L}$  level was  $\pm 0.16$ . Percent recoveries at the three levels were 89, 87, and 87%, respectively.

In a joint EPA/ASTM interlaboratory study of the cold vapor technique for total mercury in water, increments of organic and inorganic mercury were added to natural waters. Recoveries were determined by difference. A statistical summary of this study is presented in Table 1.

## 11.0 Calculations and Reporting

Calculate metal concentrations by (1) the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account.

Prepare a standard curve based on the absorbance and concentration of the mercury standards. Determine the mercury concentration in each of the sediment digests by comparing the digest absorbance with the standard calibration curve.

Mercury concentrations in water or elutriate samples should be reported in  $\mu\text{g/L}$ .

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. 17th Edition, APHA, New York, New York.

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

Kopp, J.F., M.C. Longbottom, and L.B. Lobring. 1972. Cold Vapor Method for Determining Mercury. AWWA, Vol. 64.

U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Table 1. Method Performance Data (after Kopp et al., 1972)

Number of Labs	True Values $\mu\text{g/liter}$	Mean Value $\mu\text{g/liter}$	Standard Deviation $\mu\text{g/liter}$	Accuracy as %Bias
76	0.21	0.349	0.276	66
80	0.27	0.414	0.279	53
82	0.51	0.674	0.541	32
77	0.60	0.709	0.390	18
82	3.4	3.41	1.49	0.34
79	4.1	3.81	1.12	-7.1
79	8.8	8.77	3.69	-0.4
78	9.6	9.10	3.57	-5.2

# NICKEL IN WATERS AND ELUTRIATES (ICP)

## 1.0 Scope and Application

Inductively coupled plasma atomic emission spectroscopy (ICP) determines nickel and numerous other elements that are present in aqueous samples, such as surface water and elutriate samples. The aqueous samples must first be digested with nitric acid prior to analysis.

Detection limits, sensitivity, and optimum concentration ranges for nickel, and other metals stable in a mixed standard solution with nickel, will vary with the sample aliquot size, the spectrophotometer being used, and possible matrix interferences. The data shown in Table 1 provide concentration ranges for clean aqueous samples.

The method of standard addition (MSA) shall be used for the analysis of all sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required (see section 9).

This method should only be used by spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

This procedure is based on SW-846 Methods 3010 (for digestion) and 6010 for quantitation (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

Prior to analysis, the samples to be analyzed are refluxed with nitric acid in a covered beaker. This step is repeated with additional HNO<sub>3</sub> until the final digestate is light in color and diluted to volume.

This instrumental method measures light emitted by nickel in the final digest by optical spectrometry. The digested samples are nebulized and the

resulting aerosol is transported to a plasma torch. Nickel-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes.

Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

The possibility of additional interferences named in section 3.0 should also be recognized and appropriate corrections made when necessary. The procedures that can be used for this purpose are described in section 9.

### 3.0 Interferences

There are three main forms of interferences that can occur during the analysis of water and elutriate samples by ICP. These three types of interferences include: (1) spectral, (2) physical, and (3) chemical interferences. Each is discussed separately in the following sections.

#### 3.1 Spectral Interferences

Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multi-element instruments must verify the absence of spectral interference from an element in a sample for which there is no

instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferants can be assumed.

The magnitude of the interference effects summarized in Table 2 are expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, and argon flow rate.

The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

### 3.2 Physical Interferences

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Further, it has been reported that better control of the argon flow rate improves instrument performance. Improved argon flow rate control can be accomplished with the use of mass flow controllers.

### 3.3 Chemical Interferences

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position,

etc.), buffering of the sample, matrix matching, and standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Centrifuge and centrifuge tubes.
4. Electric hot plate, adjustable and capable of maintaining a temperature of 90-95° C.
5. Inductively coupled argon plasma emission spectrometer.
6. Computer-controlled emission spectrometer with background correction.
7. Radio frequency generator.
8. Argon gas supply, welding grade or better.

### 4.2 Materials

1. Griffin beakers, 150 mL, or equivalent.
2. Watch glasses, ribbed and plain.
3. Whatman No. 41 filter paper, or equivalent.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
3. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.

- Nitric acid (1:1). Add 500 mL concentrated  $\text{HNO}_3$  to 400 mL Type II water. Dilute to 1 liter with Type II water.
- Hydrochloric acid (1:1). Add 500 mL concentrated HCl to 400 mL Type II water. Dilute to 1 liter with Type II water.
- Standard stock solutions. May be purchased or prepared from ultrahigh purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hr at  $105^\circ\text{C}$ , unless otherwise specified.

**CAUTION:** Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

- Aluminum standard stock solution ( $100\ \mu\text{g}/\text{mL}$ ). Dissolve 0.1000 g of aluminum metal in an acid mixture of 4 mL of 1:1 HCl and 1 mL of concentrated  $\text{HNO}_3$  in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of 1:1 HCl. Dilute to 1 liter with Type II water.
- Calcium standard stock solution ( $100\ \mu\text{g}/\text{mL}$ ). Suspend 0.2500 g  $\text{CaCO}_3$  dried at  $180^\circ\text{C}$  for 1 hr before weighing in Type II water and dissolve cautiously with a minimum amount of 1:1  $\text{HNO}_3$ . Add 10.0 mL of concentrated  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
- Chromium standard stock solution ( $100\ \mu\text{g}/\text{mL}$ ). Dissolve 0.1900 g  $\text{CrO}_3$  in Type II water. When solution is complete, acidify with 10 mL concentrated  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
- Potassium standard stock solution ( $100\ \mu\text{g}/\text{mL}$ ). Dissolve 0.1900 g KCl dried at  $110^\circ\text{C}$  in Type II water. Dilute to 1 liter with Type II water.
- Sodium standard stock solution ( $100\ \mu\text{g}/\text{mL}$ ). Dissolve 0.2500 g NaCl in Type II water. Add 10.0 mL concentrated  $\text{HNO}_3$ . Dilute to 1 liter with Type II water.
- Nickel standard stock solution ( $100\ \mu\text{g}/\text{mL}$ ). Dissolve 0.1000 g of nickel metal in 10.0 mL hot concentrated  $\text{HNO}_3$ . Cool. Dilute to 1 liter with Type II water.
- Mixed calibration standard solutions. Care should be taken when preparing mixed standards for ICP analysis to ensure that the elements in the final mixed standard are compatible and stable together. One set of mixed calibration standards that has been found to be useful is listed in Table 3. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities.

To prepare the mixed calibration standard for nickel, combine appropriate volumes of the individual stock solutions indicated in Table 3 in volumetric flask. Add 2 mL 1:1 HNO<sub>3</sub> and 10 mL of 1:1 HCl and dilute to 100 mL with Type II water. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see section 9.8) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Si
<u>IV</u>	<u>Al, Ca, Cr, K, Na, and Ni</u>

**NOTE:** Premixed standard solutions (traceable to NIST) containing the combined elements as listed in solutions I through IV are available from a number of commercial vendors.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Aqueous samples should be acidified to a pH of <2 with HNO<sub>3</sub>. A holding time of 6 months after sample collection is generally cited for this parameter.

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of aqueous samples to be analyzed for nickel.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Prepare a calibration blank (see section 9.4.1) and at least three mixed calibration standards in the appropriate concentration range to correlate nickel concentrations with the ICP's linear response range. Prepare standards for instrument calibration as instructed in section 5.14. Match the sample matrix and that of the standards as closely as possible.

Calibrate the instrument according to the instrument manufacturer's recommended procedures using typical mixed calibration standard solutions. Flush the system with the calibration blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

## 8.0 Procedure

1. Transfer a 100 mL representative aliquot of the well-mixed aqueous sample to a 150 mL Griffin beaker.
2. Add 3 mL of concentrated HNO<sub>3</sub>. Cover the beaker with a ribbed watch glass.
3. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL) making certain that the sample does not boil and that no portion of the beaker is allowed to go dry.

**NOTE:** If a sample is allowed to go to dryness, low recoveries may result. Should this occur, repeat the steps 1 through 3 with a fresh sample aliquot.

4. Cool the beaker and add 3 mL of concentrated HNO<sub>3</sub>.
5. Cover the beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

6. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing).
7. Uncover the beaker, or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker.
8. Add a small quantity of 1:1 HCl (10 mL/100 of final solution) and warm the beaker for an additional 15 min to dissolve any precipitate or residue resulting from evaporation.
9. Wash down the beaker walls and watch glass with Type II water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer.

**NOTE:** Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and the filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO<sub>3</sub>.

10. Adjust to the final volume of 100 mL with Type II water. The sample is now ready for analysis.
11. The analyst should follow the instructions provided by the instrument's manufacturer. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range where coordination factors are valid. The analyst must: (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.
12. Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this conditions.

13. Flush the system with the calibration blank solution for at least 1 min before the analysis of each sample. Analyze samples.

**NOTE:** Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for nickel in aqueous solutions is 25 µg/L.

The method detection limit specified in this method is sufficient to meet the Great Lakes Water Quality Criteria for nickel (260 µg/L).

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured nickel concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance of the ICP and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Blanks

Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to

correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

#### 9.4.1 Calibration Blank

The calibration blank is prepared by diluting 2 mL of 1:1 HNO<sub>3</sub> and of 1:1 HCl to 100 mL with Type II water. Prepare a sufficient quantity to flush the system between standards and samples.

The calibration blank should be analyzed prior to routine sample analysis, after every 10 samples, and at the end of the analytical run. The measured concentration in the calibration blank should be less than or equal to the method detection limit.

#### 9.4.2 Reagent Blank

The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

### 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

### 9.6 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - nickel, to the 100 mL aliquot of a routine sample for which an independent estimate of the target analyte

concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 20\%$ .

### 9.7 Interference Check Sample

The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the method detection limit for each element. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

The interference check sample should be analyzed at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Results should be within  $\pm 20\%$  of the known concentration.

### 9.8 Calibration Control Sample

A calibration control sample should be prepared in the same acid matrix as the calibration standards at 10 times the method detection limit. This sample should be prepared in accordance with the instructions provided by the supplier. The calibration control sample is used to verify the integrity of the calibration standards on a weekly basis.

### 9.9 Recommended Tests

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

### 9.9.1 Serial Dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the method detection limit after dilution), an analysis of a 1:4 dilution should agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

### 9.9.2 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 10.0 Method Performance

In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was  $9 \pm 2\%$ . The mean percent recovery of spiked elements for all wastes was  $93 \pm 6\%$ . Spike levels ranged from 100  $\mu\text{g/L}$  to 100  $\text{mg/L}$ . The wastes included sludges and industrial wastewaters.

## 11.0 Calculations and Reporting

If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in  $\mu\text{g/L}$  with up to three significant figures.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Winge, R.K., V.J. Peterson, and V.A. Fassel. 1979. Inductively coupled plasma-atomic emission spectroscopy: Prominent lines, final report, March 1977 - February 1978, Ames laboratory, Ames, IA. EPA-600/4-79-017. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Table 1. Recommended Wavelengths and Estimated Instrumental Detection Limits.

Element	Wavelength <sup>a</sup> (nm)	Estimated Detection Limit <sup>b</sup> (µg/L)
Aluminum	308.215	45
Chromium	267.716	7
Copper	324.754	6
Nickel	231.604	15
Potassium	766.491	See footnote c
Sodium	588.995	29

a - The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see section 3.1).

b - The estimated instrumental detection limits are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

c - Highly dependent on operating conditions and plasma position.

Table 2. Analyte Concentration Equivalentents arising from Interference at the 100 mg/L Level.

Analyte	Wavelength (nm)	Interferant <sup>a,b</sup>									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Mo	Tl	V
Aluminum	308.215	-	-	-	-	-	-	0.21	-	-	1.4
Calcium	317.933	-	-	0.08	-	0.01	0.01	0.04	-	0.03	0.03
Chromium	267.716	-	-	-	-	0.003	-	0.04	-	-	0.04
Nickel	231.604	-	-	-	-	-	-	-	-	-	-
Sodium	588.995	0.30	-	-	-	-	-	-	-	-	-

a - Dashes indicate that no interference was observed even when interferants were introduced at the following levels:

Al - 1000 mg/L,  
 Ca - 1000 mg/L,  
 Cr - 200 mg/L,  
 Cu - 200 mg/L,  
 Fe - 1000 mg/L,  
 Mg - 1000 mg/L,  
 Mn - 200 mg/L,  
 Tl - 200 mg/L,  
 V - 200 mg/L, and

b - The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

Table 4. ICP Precision and Accuracy Data<sup>a</sup>

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)
Cr	150	149	3.8	10	10	18	50	50	3.3
Al	700	695	5.6	60	62	33	160	161	13
Ni	250	245	5.8	30	28	11	60	55	14

a - Not all elements were analyzed by all laboratories.

b - SD = standard deviation.

# LEAD IN WATERS AND ELUTRIATES (ICP)

## 1.0 Scope and Application

Inductively coupled plasma atomic emission spectroscopy (ICP) determines lead and numerous other elements that are present in aqueous samples, such as surface water and elutriate samples. The aqueous samples must first be digested with nitric acid prior to analysis.

Detection limits, sensitivity, and optimum concentration ranges for lead, and other metals stable in a mixed standard solution with lead, will vary with the sample aliquot size, the spectrophotometer being used, and possible matrix interferences. The data shown in Table 1 provide concentration ranges for clean aqueous samples.

The method of standard addition (MSA) shall be used for the analysis of all sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required (see section 9).

This method should only be used by spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

This procedure is based on SW-846 Methods 3010 (for digestion) and 6010 for quantitation (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

Prior to analysis, the samples to be analyzed are refluxed with nitric acid in a covered beaker. This step is repeated with additional HNO<sub>3</sub> until the final digestate is light in color and diluted to volume.

This instrumental method measures light emitted by lead in the final digest by optical spectrometry. The digested samples are nebulized and the

resulting aerosol is transported to a plasma torch. Lead-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes.

Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

The possibility of additional interferences named in section 3.0 should also be recognized and appropriate corrections made when necessary. The procedures that can be used for this purpose are described in section 9.

### 3.0 Interferences

There are three main forms of interferences that can occur during the analysis of water and elutriate samples by ICP. These three types of interferences include: (1) spectral, (2) physical, and (3) chemical interferences. Each is discussed separately in the following sections.

#### 3.1 Spectral Interferences

Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multi-element instruments must verify the absence of spectral interference from an element in a sample for which there is no

instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferants can be assumed.

The magnitude of the interference effects summarized in Table 2 are expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that Pb is to be determined (at 220.353 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for Pb equivalent to approximately 0.17 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for Pb equivalent to approximately 0.017 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, and argon flow rate.

The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

### 3.2 Physical Interferences

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Further, it has been reported that better control of the argon flow rate improves instrument performance. Improved argon flow rate control can be accomplished with the use of mass flow controllers.

### 3.3 Chemical Interferences

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, etc.), buffering of the sample, matrix matching, and standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Centrifuge and centrifuge tubes.
4. Electric hot plate, adjustable and capable of maintaining a temperature of 90-95° C.
5. Inductively coupled argon plasma emission spectrometer.
6. Computer-controlled emission spectrometer with background correction.
7. Radio frequency generator.
8. Argon gas supply, welding grade or better.

### 4.2 Materials

1. Griffin beakers, 150 mL, or equivalent.
2. Watch glasses, ribbed and plain.
3. Whatman No. 41 filter paper, or equivalent.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will

- interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
3. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
  4. Nitric acid (1:1). Add 500 mL concentrated HNO<sub>3</sub> to 400 mL Type II water. Dilute to 1 liter with Type II water.
  5. Hydrochloric acid (1:1). Add 500 mL concentrated HCl to 400 mL Type II water. Dilute to 1 liter with Type II water.
  6. Standard stock solutions. May be purchased or prepared from ultrahigh purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hr at 105° C, unless otherwise specified.

**CAUTION:** Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

7. Beryllium standard stock solution (100 µg/mL). Dissolve 1.970 g BeSO<sub>4</sub>·4H<sub>2</sub>O (analytical reagent grade, undried), in 100 mL of Type II water, add 10.0 ml concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
8. Cadmium standard stock solution (100 µg/mL). Dissolve 0.1100 g CdO (analytical reagent grade) in a minimum amount of 1:1 HNO<sub>3</sub>. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
9. Lead standard stock solution (100 µg/mL). Dissolve 0.1600 g Pb(NO<sub>3</sub>)<sub>2</sub> (analytical reagent grade) in a minimum amount of 1:1 HNO<sub>3</sub>. Add 10 mL 1:1 HNO<sub>3</sub>. Add 10 mL 1:1 HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
10. Manganese standard stock solution (100 µg/mL). Dissolve 0.1000 g of manganese metal, in an acid mixture of 10 mL concentrated HCl and 1 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
11. Selenium standard stock solution (100 µg/mL). Dissolve 0.1700 g H<sub>2</sub>SeO<sub>3</sub> (analytical reagent grade, undried) in 100 mL of Type II water. Dilute to 1 liter with Type II water.
12. Zinc standard stock solution (100 µg/mL). Dissolve 0.1200 g ZnO in a minimum amount of 1:1 HNO<sub>3</sub>. Add 10.0 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
13. Mixed calibration standard solutions. Care should be taken when preparing mixed standards for ICP analysis to ensure that the elements in the final mixed standard are compatible and stable

together. One set of mixed calibration standards that has been found to be useful is listed in Table 3. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities.

To prepare the mixed calibration standard for lead, combine appropriate volumes of the individual stock solutions indicated in Table 3 in volumetric flask. Add 2 mL 1:1 HNO<sub>3</sub> and 10 mL of 1:1 HCl and dilute to 100 mL with Type II water. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see section 9.8) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Si
IV	Al, Ca, Cr, K, Na, and Ni

**NOTE:** Premixed standard solutions (traceable to NIST) containing the combined elements as listed in solutions I through IV are available from a number of commercial vendors.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Aqueous samples should be acidified to a pH of <2 with HNO<sub>3</sub>. A holding time of 6 months after sample collection is generally cited for this parameter.

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of aqueous samples to be analyzed for lead.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Prepare a calibration blank (see section 9.4.1) and at least three mixed calibration standards in the appropriate concentration range to correlate lead concentrations with the ICP's linear response range. Prepare standards for instrument calibration as instructed in section 5.13. Match the sample matrix and that of the standards as closely as possible.

Calibrate the instrument according to the instrument manufacturer's recommended procedures using typical mixed calibration standard solutions. Flush the system with the calibration blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

## 8.0 Procedure

1. Transfer a 100 mL representative aliquot of the well-mixed aqueous sample to a 150 mL Griffin beaker.
2. Add 3 mL of concentrated HNO<sub>3</sub>. Cover the beaker with a ribbed watch glass.
3. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL) making certain that the sample does not boil and that no portion of the beaker is allowed to go dry.

**NOTE:** If a sample is allowed to go to dryness, low recoveries may result. Should this occur, repeat the steps 1 through 3 with a fresh sample aliquot.

4. Cool the beaker and add 3 mL of concentrated HNO<sub>3</sub>.

5. Cover the beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.
6. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing).
7. Uncover the beaker, or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker.
8. Add a small quantity of 1:1 HCl (10 mL/100 of final solution) and warm the beaker for an additional 15 min to dissolve any precipitate or residue resulting from evaporation.
9. Wash down the beaker walls and watch glass with Type II water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer.

**NOTE:** Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and the filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO<sub>3</sub>.

10. Adjust to the final volume of 100 mL with Type II water. The sample is now ready for analysis.
11. The analyst should follow the instructions provided by the instrument's manufacturer. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range where coordination factors are valid. The analyst must: (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.
12. Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5%

(or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this conditions.

13. Flush the system with the calibration blank solution for at least 1 min before the analysis of each sample. Analyze samples.

**NOTE:** Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for lead in aqueous solutions is 50 µg/L.

The method detection limit specified in this method is sufficient to meet the Great Lakes Water Quality Criteria for lead (82 µg/L).

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured lead concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance of the ICP and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be ± 15% of the known value or within the certified value provided by the supplier, whichever is larger.

## 9.4 Blanks

Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

### 9.4.1 Calibration Blank

The calibration blank is prepared by diluting 2 mL of 1:1 HNO<sub>3</sub> and of 1:1 HCl to 100 mL with Type II water. Prepare a sufficient quantity to flush the system between standards and samples.

The calibration blank should be analyzed prior to routine sample analysis, after every 10 samples, and at the end of the analytical run. The measured concentration in the calibration blank should be less than or equal to the method detection limit.

### 9.4.2 Reagent Blank

The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.6 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - lead, to the 100 mL aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 20\%$ .

## 9.7 Interference Check Sample

The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the method detection limit for each element. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

The interference check sample should be analyzed at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Results should be within  $\pm 20\%$  of the known concentration.

## 9.8 Calibration Control Sample

A calibration control sample should be prepared in the same acid matrix as the calibration standards at 10 times the method detection limit. This sample should be prepared in accordance with the instructions provided by the supplier. The calibration control sample is used to verify the integrity of the calibration standards on a weekly basis.

## 9.9 Recommended Tests

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration

data for analyte elements. These tests will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

### 9.9.1 Serial Dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the method detection limit after dilution), an analysis of a 1:4 dilution should agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

### 9.9.2 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.

3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 10.0 Method Performance

In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was  $9 \pm 2\%$ . The mean percent recovery of spiked elements for all wastes was  $93 \pm 6\%$ . Spike levels ranged from 100  $\mu\text{g/L}$  to 100  $\text{mg/L}$ . The wastes included sludges and industrial wastewaters.

## 11.0 Calculations and Reporting

If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in  $\mu\text{g/L}$  with up to three significant figures.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055. U.S. Environmental Protection Agency, Washington, D.C.

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Winge, R.K., V.J. Peterson, and V.A. Fassel. 1979. Inductively coupled plasma-atomic emission spectroscopy: Prominent lines, final report, March 1977 - February 1978, Ames laboratory, Ames, IA. EPA-600/4-79-017. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Table 1. Recommended Wavelengths and Estimated Instrumental Detection Limits.

Element	Wavelength <sup>a</sup> (nm)	Estimated Detection Limit <sup>b</sup> (µg/L)
Beryllium	313.042	0.3
Cadmium	226.502	4
Lead	220.353	42
Manganese	257.610	2
Selenium	196.026	75
Zinc	213.856	2

a - The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see section 3.1).

b - The estimated instrumental detection limits are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

Table 2. Analyte Concentration Equivalentents arising from Interference at the 100 mg/L Level.

Analyte	Wavelength (nm)	Interferant <sup>a,b</sup>									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Mi	Tl	V
Beryllium	313.042	-	-	-	-	-	-	-	-	0.04	0.05
Cadmium	226.502	-	-	-	-	0.03	-	-	0.02	-	-
Lead	220.353	0.17	-	-	-	-	-	-	-	-	-
Manganese	257.610	0.005	-	0.01	-	0.002	0.002	-	-	-	-
Selenium	196.026	0.23	-	-	-	0.09	-	-	-	-	-
Zinc	213.856	-	-	-	0.14	-	-	-	0.29	-	-

a - Dashes indicate that no interference was observed even when interferants were introduced at the following levels:

Al - 1000 mg/L,  
 Ca - 1000 mg/L,  
 Cr - 200 mg/L,  
 Cu - 200 mg/L,  
 Fe - 1000 mg/L,  
 Mg - 1000 mg/L,  
 Mn - 200 mg/L,  
 Tl - 200 mg/L,  
 V - 200 mg/L, and

b - The figures recorded as analyte concentrations are not the actual observed concentrations. To obtain those figures, add the listed concentration to the interferant figure.

Table 4. ICP Precision and Accuracy Data<sup>a</sup>

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
Cd	50	48	12	2.5	2.9	16	14	13	16
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se <sup>c</sup>	40	32	21.9	6	8.5	42	10	8.5	8.3

a - Not all elements were analyzed by all laboratories.

b - SD = standard deviation.

c - Results for Se are from two laboratories.

# ZINC IN WATERS AND ELUTRIATES (ICP)

## 1.0 Scope and Application

Inductively coupled plasma atomic emission spectroscopy (ICP) determines zinc and numerous other elements that are present in aqueous samples, such as surface water and elutriate samples. The aqueous samples must first be digested with nitric acid prior to analysis.

Detection limits, sensitivity, and optimum concentration ranges for zinc, and other metals stable in a mixed standard solution with zinc, will vary with the sample aliquot size, the spectrophotometer being used, and possible matrix interferences. The data shown in Table 1 provide concentration ranges for clean aqueous samples.

The method of standard addition (MSA) shall be used for the analysis of all sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required (see section 9).

This method should only be used by spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

This procedure is based on SW-846 Methods 3010 (for digestion) and 6010 for quantitation (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

Prior to analysis, the samples to be analyzed are refluxed with nitric acid in a covered beaker. This step is repeated with additional HNO<sub>3</sub> until the final digestate is light in color and diluted to volume.

This instrumental method measures light emitted by zinc in the final digest by optical spectrometry. The digested samples are nebulized and the resulting

aerosol is transported to a plasma torch. Zinc-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes.

Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

The possibility of additional interferences named in section 3.0 should also be recognized and appropriate corrections made when necessary. The procedures that can be used for this purpose are described in section 9.

### 3.0 Interferences

There are three main forms of interferences that can occur during the analysis of water and elutriate samples by ICP. These three types of interferences include: (1) spectral, (2) physical, and (3) chemical interferences. Each is discussed separately in the following sections.

#### 3.1 Spectral Interferences

Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multi-element instruments must verify the absence of spectral interference from an element in a sample for which there is no

instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferants can be assumed.

The magnitude of the interference effects summarized in Table 2 are expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that Zn is to be determined (at 213.856 nm) in a sample containing approximately 10 mg/L of Cu. According to Table 2, 100 mg/L of Cu would yield a false signal for Zn equivalent to approximately 0.14 mg/L. Therefore, the presence of 10 mg/L of Cu would result in a false signal for Zn equivalent to approximately 0.014 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, and argon flow rate.

The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

### 3.2 Physical Interferences

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Further, it has been reported that better control of the argon flow rate improves instrument performance. Improved argon flow rate control can be accomplished with the use of mass flow controllers.

### 3.3 Chemical Interferences

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, etc.), buffering of the sample, matrix matching, and standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Centrifuge and centrifuge tubes.
4. Electric hot plate, adjustable and capable of maintaining a temperature of 90-95° C.
5. Inductively coupled argon plasma emission spectrometer.
6. Computer-controlled emission spectrometer with background correction.
7. Radio frequency generator.
8. Argon gas supply, welding grade or better.

### 4.2 Materials

1. Griffin beakers, 150 mL, or equivalent.
2. Watch glasses, ribbed and plain.
3. Whatman No. 41 filter paper, or equivalent.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will

- interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
3. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
  4. Nitric acid (1:1). Add 500 mL concentrated HNO<sub>3</sub> to 400 mL Type II water. Dilute to 1 liter with Type II water.
  5. Hydrochloric acid (1:1). Add 500 mL concentrated HCl to 400 mL Type II water. Dilute to 1 liter with Type II water.
  6. Standard stock solutions. May be purchased or prepared from ultrahigh purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hr at 105° C, unless otherwise specified.

**CAUTION:** Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

7. Beryllium standard stock solution (100 µg/mL). Dissolve 1.970 g BeSO<sub>4</sub>·4H<sub>2</sub>O (analytical reagent grade, undried), in 100 mL of Type II water, add 10.0 ml concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
8. Cadmium standard stock solution (100 µg/mL). Dissolve 0.1100 g CdO (analytical reagent grade) in a minimum amount of 1:1 HNO<sub>3</sub>. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
9. Lead standard stock solution (100 µg/mL). Dissolve 0.1600 g Pb(NO<sub>3</sub>)<sub>2</sub> (analytical reagent grade) in a minimum amount of 1:1 HNO<sub>3</sub>. Add 10 mL 1:1 HNO<sub>3</sub>. Add 10 mL 1:1 HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
10. Manganese standard stock solution (100 µg/mL). Dissolve 0.1000 g of manganese metal, in an acid mixture of 10 mL concentrated HCl and 1 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
11. Selenium standard stock solution (100 µg/mL). Dissolve 0.1700 g H<sub>2</sub>SeO<sub>3</sub> (analytical reagent grade, undried) in 100 mL of Type II water. Dilute to 1 liter with Type II water.
12. Zinc standard stock solution (100 µg/mL). Dissolve 0.1200 g ZnO in a minimum amount of 1:1 HNO<sub>3</sub>. Add 10.0 mL concentrated HNO<sub>3</sub>. Dilute to 1 liter with Type II water.
13. Mixed calibration standard solutions. Care should be taken when preparing mixed standards for ICP analysis to ensure that the elements in the final mixed standard are compatible and stable

together. One set of mixed calibration standards that has been found to be useful is listed in Table 3. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities.

To prepare the mixed calibration standard for zinc, combine appropriate volumes of the individual stock solutions indicated in Table 3 in volumetric flask. Add 2 mL 1:1 HNO<sub>3</sub> and 10 mL of 1:1 HCl and dilute to 100 mL with Type II water. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see section 9.8) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Si
IV	Al, Ca, Cr, K, Na, and Ni

**NOTE:** Premixed standard solutions (traceable to NIST) containing the combined elements as listed in solutions I through IV are available from a number of commercial vendors.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Aqueous samples should be acidified to a pH of <2 with HNO<sub>3</sub>. A holding time of 6 months after sample collection is generally cited for this parameter.

All sample containers must be prewashed with detergents, acids, and Type II water. Either glass or plastic containers can be used for the storage of aqueous samples to be analyzed for zinc.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Prepare a calibration blank (see section 9.4.1) and at least three mixed calibration standards in the appropriate concentration range to correlate zinc concentrations with the ICP's linear response range. Prepare standards for instrument calibration as instructed in section 5.13. Match the sample matrix and that of the standards as closely as possible.

Calibrate the instrument according to the instrument manufacturer's recommended procedures using typical mixed calibration standard solutions. Flush the system with the calibration blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

## 8.0 Procedure

1. Transfer a 100 mL representative aliquot of the well-mixed aqueous sample to a 150 mL Griffin beaker.
2. Add 3 mL of concentrated HNO<sub>3</sub>. Cover the beaker with a ribbed watch glass.
3. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL) making certain that the sample does not boil and that no portion of the beaker is allowed to go dry.

**NOTE:** If a sample is allowed to go to dryness, low recoveries may result. Should this occur, repeat the steps 1 through 3 with a fresh sample aliquot.

4. Cool the beaker and add 3 mL of concentrated HNO<sub>3</sub>.

5. Cover the beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.
6. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing).
7. Uncover the beaker, or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker.
8. Add a small quantity of 1:1 HCl (10 mL/100 of final solution) and warm the beaker for an additional 15 min to dissolve any precipitate or residue resulting from evaporation.
9. Wash down the beaker walls and watch glass with Type II water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer.

**NOTE:** Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and the filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO<sub>3</sub>.

10. Adjust to the final volume of 100 mL with Type II water. The sample is now ready for analysis.
11. The analyst should follow the instructions provided by the instrument's manufacturer. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range where coordination factors are valid. The analyst must: (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.
12. Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5%

(or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this conditions.

13. Flush the system with the calibration blank solution for at least 1 min before the analysis of each sample. Analyze samples.

**NOTE:** Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for zinc in aqueous solutions is 20 µg/L.

The method detection limit specified in this method is sufficient to meet the Great Lakes Water Quality Criteria for zinc (67 µg/L).

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured zinc concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance of the ICP and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

## 9.4 Blanks

Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

### 9.4.1 Calibration Blank

The calibration blank is prepared by diluting 2 mL of 1:1 HNO<sub>3</sub> and of 1:1 HCl to 100 mL with Type II water. Prepare a sufficient quantity to flush the system between standards and samples.

The calibration blank should be analyzed prior to routine sample analysis, after every 10 samples, and at the end of the analytical run. The measured concentration in the calibration blank should be less than or equal to the method detection limit.

### 9.4.2 Reagent Blank

The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.6 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - zinc, to the 100 mL aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 20\%$ .

## 9.7 Interference Check Sample

The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the method detection limit for each element. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

The interference check sample should be analyzed at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Results should be within  $\pm 20\%$  of the known concentration.

## 9.8 Calibration Control Sample

A calibration control sample should be prepared in the same acid matrix as the calibration standards at 10 times the method detection limit. This sample should be prepared in accordance with the instructions provided by the supplier. The calibration control sample is used to verify the integrity of the calibration standards on a weekly basis.

## 9.9 Recommended Tests

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration

data for analyte elements. These tests will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

### 9.9.1 Serial Dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the method detection limit after dilution), an analysis of a 1:4 dilution should agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

### 9.9.2 Standard Addition

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method in which two identical aliquots of the sample solution, each of a known volume ( $V_x$ ), are taken. To the first aliquot (labeled A), add a small volume ( $V_s$ ) of a standard analyte solution of known concentration ( $C_s$ ). To the second aliquot (labeled B), add the same volume ( $V_s$ ) of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration ( $C_x$ ) is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where  $S_A$  and  $S_B$  are the analytical signals (corrected for the blank) of solutions A and B, respectively.  $V_s$  and  $C_s$  should be chosen so that  $S_A$  is roughly twice  $S_B$  on the average. It is best if  $V_s$  is made much less than  $V_x$  and thus  $C_s$  is much greater than  $C_x$ , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.

3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

## 10.0 Method Performance

In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was  $9 \pm 2\%$ . The mean percent recovery of spiked elements for all wastes was  $93 \pm 6\%$ . Spike levels ranged from 100  $\mu\text{g/L}$  to 100  $\text{mg/L}$ . The wastes included sludges and industrial wastewaters.

## 11.0 Calculations and Reporting

If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in  $\mu\text{g/L}$  with up to three significant figures.

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Zinc	213.856	2

a - The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see section 3.1).

b - The estimated instrumental detection limits are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

Table 2. Analyte Concentration Equivalentents arising from Interference at the 100 mg/L Level.

Analyte	Wavelength (nm)	Interferant <sup>a,b</sup>									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Mi	Tl	V
Beryllium	313.042	-	-	-	-	-	-	-	-	0.04	0.05
Cadmium	226.502	-	-	-	-	0.03	-	-	0.02	-	-
Lead	220.353	0.17	-	-	-	-	-	-	-	-	-
Manganese	257.610	0.005	-	0.01	-	0.002	0.002	-	-	-	-
Selenium	196.026	0.23	-	-	-	0.09	-	-	-	-	-
Zinc	213.856	-	-	-	0.14	-	-	-	0.29	-	-

a - Dashes indicate that no interference was observed even when interferants were introduced at the following levels:

Al - 1000 mg/L,  
 Ca - 1000 mg/L,  
 Cr - 200 mg/L,  
 Cu - 200 mg/L,  
 Fe - 1000 mg/L,  
 Mg - 1000 mg/L,  
 Mn - 200 mg/L,  
 Tl - 200 mg/L,  
 V - 200 mg/L, and

b - The figures recorded as analyte concentrations are not the actual observed concentrations. To obtain those figures, add the listed concentration to the interferant figure.

Table 4. ICP Precision and Accuracy Data<sup>a</sup>

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)	True Value (µg/L)	Mean Reported Value (µg/L)	Mean SD <sup>b</sup> (%)
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
Cd	50	48	12	2.5	2.9	16	14	13	16
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se <sup>c</sup>	40	32	21.9	6	8.5	42	10	8.5	8.3

a - Not all elements were analyzed by all laboratories.

b - SD = standard deviation.

c - Results for Se are from two laboratories.

# TOTAL PETROLEUM HYDROCARBONS IN WATERS AND ELUTRIATES (SPECTROPHOTOMETRIC, INFRARED)

## 1.0 Scope and Application

This method is appropriate for the determination of fluorocarbon-113 extractable petroleum hydrocarbons from surface waters and sediment elutriates. It should be noted that this method will change upon identification and approval of an environmentally friendly solvent.

The method is applicable to measurement of light fuels, although loss of about half of any gasoline present during the extraction manipulations can be expected.

The method is appropriate for a total petroleum hydrocarbon concentration of 1 mg/L or less.

This method is based on EPA Method 418.1 (USEPA, 1983).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

The sample is acidified to a low pH (<2) and serially extracted with fluorocarbon-113 in a separatory funnel. Interferences that may be co-extracted with the total petroleum hydrocarbons (TPHs) are removed with silica gel adsorbent. Infrared analysis of the extract is performed at  $2930\text{ cm}^{-1}$  and TPH concentrations determined by direct comparison with standards.

## 3.0 Interferences

Total petroleum hydrocarbons (TPHs) are operationally defined by the extraction procedure and the analytical technique. Petroleum fuels, from gasoline through No. 2 fuel oils, may be lost during sample preparation.

The method is not considered applicable to light hydrocarbons that volatilize below 70° C. Also, some crude oils and heavy fuel oils that are not soluble in fluorocarbon-113 will have low recoveries.

The rate and time of extraction in the Soxhlet apparatus should be strictly controlled because of varying solubilities of different greases.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Infrared spectrophotometer, scanning or fixed wavelength, for measurement around 2930  $\text{cm}^{-1}$ .
4. Magnetic stirrer, with Teflon coated stirring bars.
5. Mortar and pestle.
6. Soxhlet extraction apparatus.
7. Vacuum pump or other source of vacuum.

### 4.2 Materials

1. Separatory funnel with Teflon stopcock, 2000 mL.
2. Beakers, glass, 150 mL.
3. Cells, 10 mm, 50 mm, and 100 mm pathlength, sodium chloride or infrared grade glass.
4. Extraction thimbles, paper.
5. Glass bottles with stoppers, 50 mL.
6. Glass wool or beads.
7. Volumetric flasks, class A, 200 mL.
8. Volumetric flasks, class A, 100 mL.
9. Whatman filter paper No. 40, 11 cm.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.

2. Fluorocarbon-113 (1,1,2-trichloro-1,2,2-trifluoroethane), boiling point 47° C.

**NOTE:** The solvent should leave no measurable residue on evaporation. Redistill if necessary.

3. Concentrated hydrochloric acid (HCl), reagent grade. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
4. Hydrochloric acid (HCl), 1:1. Mix equal volumes of concentrated HCl and Type II water.
5. Silica gel, 60-200 mesh, Davidson Grade 950, or equivalent. Should contain 1-2% water as defined by residue test at 130° C. Adjust by overnight equilibration, if needed.
6. Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), anhydrous crystal.
7. Reference oil used for calibration mixtures. Pipet 15.0 mL n-hexadecane ( $\text{C}_{16}\text{H}_{34}$ ), 15.0 mL isooctane ( $\text{C}_8\text{H}_{18}$ ), and 10.0 mL chlorobenzene ( $\text{C}_6\text{H}_5\text{Cl}$ ) into a 50 mL glass-stoppered bottle. Maintain the integrity of the mixture by keeping stoppered except when withdrawing aliquots.
8. Reference oil stock solution. Pipet 1.0 mL reference oil into a tared 200 mL volumetric flask and immediately stopper. Weigh and dilute to volume with fluorocarbon-113.
9. Reference oil working standards. Pipet appropriate volumes of stock standard into 100 mL volumetric flasks according to the cell pathlength to be used. Dilute to volume with fluorocarbon-113. Calculate concentration of standards from the stock standard.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Because losses of grease can occur on sampling equipment, the collection of composite samples is impractical for this parameter.

Samples should be preserved with 5 mL 1:1 HCl at the time of collection to a pH of <2. A holding time of 28 days after sample collection is generally cited for this parameter.

The sample should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Sample aliquots to be analyzed for TPH should be collected and stored in 1 L glass bottles.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Select appropriate working standards and cell pathlength based on the expected total petroleum hydrocarbon concentration in the aqueous solution. The following information is presented as a guide for selecting a suitable cell pathlength:

<u>Pathlength</u>	<u>Range</u>
10 mm	2-40 mg
50 mm	0.5-8 mg
100 mm	0.1-4 mg

Calibrate the instrument for the appropriate cells using a series of working standards. It is not necessary to add silica gel to the standards.

Scan the standards from 3200 to 2700  $\text{cm}^{-1}$  using a scanning infrared spectrophotometer. Fluorocarbon-113 should be used in the reference beam of a dual beam instrument or to zero a single beam instrument. The absorbance of the 2930  $\text{cm}^{-1}$  peak should be used to construct a standard curve.

## 8.0 Procedure

1. Mark the water meniscus level on the sample bottle containing the original sample for later determination of the sample volume.

2. If the sample was not acidified at time of collection, add 5 mL 1:1 hydrochloric acid to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.
3. Pour the sample into a 2000 mL separatory funnel.
4. Add 30 mL fluorocarbon-113 to the sample bottle and rotate the bottle to rinse the sides.
5. Transfer the solvent into the separatory funnel.
6. Extract by shaking vigorously for 2 minutes. Allow the layers to separate.
7. Filter the solvent layer through a funnel containing solvent-moistened filter paper into a 100 mL volumetric flask.

**NOTE:** An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate into the filter paper cone and slowly draining the emulsion through the salt. Additional 1 g portions can be added to the cone as required.

8. Repeat steps 4 through 7 twice more with 30 mL portions of fresh solvent, combining all solvent into the volumetric flask.
9. Rinse the tip of the separatory funnel, filter paper, and the funnel with a total of 5-10 mL solvent and collect the rinsings in the flask.
10. Dilute the extract to 100 mL with fluorocarbon-113.

**NOTE:** If the extract is known to contain greater than 100 mg of non-hydrocarbon organic material, pipet an appropriate portion of the sample to a 100 mL volumetric and dilute to volume.

11. Discard about 5-10 mL solution from the volumetric flask. Add 3 g silica gel and a stirring bar.
12. Stopper the volumetric flask and stir the solution for a minimum of 5 min on a magnetic stirrer.
13. After the silica gel has settled in the sample extract, fill a clean cell with solution and determine the absorbance of the extract.

**NOTE:** If the absorbance exceeds 0.8, prepare an appropriate dilution and reanalyze the sample.

**NOTE:** The possibility that the absorptive capacity of the silica gel has been exceeded can be tested at this point by adding another 3.0 g silica gel to the extract and repeating the treatment and determination.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for TPH in aqueous solutions is 100 µg/L.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured TPH concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the instrument detection limit.

### 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.6 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte (i.e., reference oil), in this case - TPH, to the 20 g aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have a relative percent difference (RPD) of  $\leq 20\%$ .

## 10.0 Method Performance

When a sewage sample containing 12.6 mg/L oil and grease was spiked with 14.0 mg of a mixture containing No. 2 fuel oil and Wesson oil and analyzed by a single laboratory, the recovery was 93% with a standard deviation of 0.9 mg/L.

In a second study, sewage containing 17.5 mg/L oil and grease was spiked with 14 mg of a mixture containing No. 2 fuel oil and Wesson oil. The recovery was 99% and the standard deviation was 1.4 mg/L.

## 11.0 Calculations and Reporting

Determine the concentration of petroleum hydrocarbons in the extract by comparing the response against the calibration plot. Calculate the concentration of petroleum hydrocarbons in the original sample using the following formula:

$$\text{TPH, mg/L} = \frac{R \times D}{V}$$

where:

R = TPH as determined from the calibration plot, mg.

D = extract dilution factor, if used.

V = volume of sample, L.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

Blum, K.A. and M.J. Taras. 1968. Determination of Emulsifying Oil in Industrial Wastewater" JWPCF Research Supplement 40:R404.

U.S. Environmental Protection Agency. 1983. Methods for the Chemical Analysis of Water and Wastes. EPA-600/4-79-020. U.S. Environmental Protection Agency Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

# PHENOLICS IN WATERS AND ELUTRIATES (COLORIMETRIC, AUTOMATED 4-AAP)

## 1.0 Scope and Application

This method is applicable to the determination of phenolic compounds in surface water samples and sediment elutriates. The method is capable of measuring phenolic materials over a range of 2 to 500  $\mu\text{g/L}$  in aqueous samples when using phenol as a standard.

This method is based on SW-846 Method 9066 (EPA, 1986).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

Phenolic compounds are separated from the original sample matrix by distillation under acidic conditions ( $\text{pH} < 4.0$ ). The phenolic compounds in the distillate are then reacted with alkaline ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ) and 4-aminoantipyrine (4-AAP) to form a red complex which is measured at 505 or 520  $\text{nm}$ .

## 3.0 Interferences

Interferences from sulfur compounds are eliminated by acidifying the sample to a  $\text{pH}$  of  $< 4.0$  with  $\text{H}_2\text{SO}_4$  and aerating briefly by stirring.

Color and turbidity in the original sample can interfere with this colorimetric procedure. Color interference is eliminated by distilling the phenolic compounds from the original sample prior to analysis. Turbidity is removed by sample filtration prior to analysis.

Oxidizing agents, such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate (see section 5.0, item 3). If chlorine is not removed, the phenolic compounds may be partially oxidized and the sample results may be biased low.

Background contamination from plastic tubing and sample containers is eliminated by filling the wash receptacle by siphon (using Kel-F tubing) and using glass tubes for the samples and standards.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.01 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Distillation apparatus, all glass, consisting of a 1-liter pyrex distillation flask and a Graham condenser.
4. pH meter.
5. Automated continuous-flow analytical instrument with:
  - a. sampler equipped with continuous mixer,
  - b. manifold,
  - c. proportioning pump II or III,
  - d. heating bath with distillation coil,
  - e. distillation head,
  - f. colorimeter equipped with a 50 mm flowcell and 505 or 520 nm filter, and
  - g. recorder.

### 4.2 Materials

1. Volumetric flasks, class A, 1 L.
2. Volumetric flasks, class A, 100 mL.

## 5.0 Reagents

1. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
2. 4-Aminoantipyrine (4-AAP). Dissolve 0.65 g of 4-aminoantipyrine in 800 mL of Type II water. Dilute to 1 liter with Type II water. Prepare fresh daily.
3. Ferrous ammonium sulfate ( $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ). Dissolve 1.1 g ferrous ammonium sulfate in 500 mL of Type II water containing 1 mL

concentrated  $\text{H}_2\text{SO}_4$ . Dilute to 1 liter with freshly boiled and cooled Type II water.

4. Buffered potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ). Dissolve 2.0 g potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ), 3.1 g boric acid ( $\text{H}_3\text{BO}_3$ ), and 3.75 g potassium chloride (KCl) in 800 mL of Type II water. Adjust to pH of 10.3 with 1 N sodium hydroxide. Dilute to 1 liter with Type II water. Add 0.5 mL of Brij-35 (available from Technicon). Prepare fresh weekly.

**NOTE:** Brij-35 is a wetting agent and is a proprietary Technicon product.

5. Sodium hydroxide (NaOH), 1 N. Dissolve 40 g NaOH in 500 mL of Type II water. Cool. Dilute to 1 liter with Type II water.
6. Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ), reagent grade. Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
7. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), 1 N. Add 28 mL concentrated  $\text{H}_2\text{SO}_4$  to 900 mL of Type II water. Dilute to 1 liter with Type II water.
8. Phenol stock solution. Dissolve 1.00 g phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) in 500 mL of Type II water. Dilute to 1 liter with Type II water. Add 0.5 mL concentrated  $\text{H}_2\text{SO}_4$  as preservative (1.0 mg/mL phenol).

**CAUTION:** This solution is toxic.

9. Phenol standard solution A. Dilute 10.0 mL of phenol stock solution to 1 liter with Type II water (0.01 mg/mL phenol).
10. Phenol standard solution B. Dilute 100.0 mL of phenol standard solution A to 1 liter with Type II water (0.001 mg/mL phenol).
11. Phenol standard solution C. Dilute 100.00 mL of phenol standard solution B to 1 liter with Type II water (0.0001 mg/mL phenol).

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Biological degradation of phenolic compounds is inhibited by acidification to a pH <2 with H<sub>2</sub>SO<sub>4</sub>. A holding time of 28 days after sample collection is generally cited for this parameter.

The sample should be stored under refrigerated conditions (4° C).

All sample containers must be prewashed with detergents, acids, and Type II water. Sample aliquots to be analyzed for phenolic compounds should be collected and stored in glass bottles.

## 7.0 Calibration and Standardization

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

Calibration curves must be composed of a minimum of a blank and three standards. A separate calibration curve should be prepared for every hour of continuous sample analysis.

Using standard solution A, B, or C, prepare the following standards in 100 mL volumetric flasks:

<u>Standard Solution (mL)</u>	<u>Concentration (µg/L)</u>
<u>Solution C</u>	
1.0	1.0
2.0	2.0
3.0	3.0
5.0	5.0
<u>Solution B</u>	
1.0	10.0
2.0	20.0
5.0	50.0
10.0	100.0
<u>Solution A</u>	
2.0	200.0
3.0	300.0
5.0	500.0

Each standard should be preserved by adding 2 drops of concentrated  $\text{H}_2\text{SO}_4$  to 100.0 mL.

Prepare a linear standard curve by plotting peak heights of standards against concentration values.

## 8.0 Procedure

1. Place 500 mL of sample into a 1-L pyrex distillation flask.
2. Adjust the pH of the sample to approximately 4 with the addition of 1 N sulfuric acid.
3. Attach the condenser and distill over 450 mL of distillate.
4. When boiling has ceased in the distillation flask, add 50 mL warm Type II water to the distillation flask and resume sample distillation until a total of 500 mL distillate has been collected.
5. Acidify the distillates with 2 drops concentrated  $\text{H}_2\text{SO}_4$  per 100 mL.

**NOTE:** If the sample distillate is turbid, it should be filtered through a prewashed membrane filter prior to analysis.

6. Set up a AutoAnalyzer manifold with the following flow rates:

Air	0.32 mL/min.
Sample	2.00 mL/min.
Distilling solution	0.42 mL/min.
Waste from still	0.42 mL/min.
Air	0.32 mL/min.
Resample waste	1.00 mL/min.
Resample	1.2 mL/min.
4-AAP	0.23 mL/min.
Buffered potassium ferricyanide	0.23 mL/min.
Waste from F/C	1.0 mL/min.

7. Fill the wash receptacle by siphon. Use Kel-F tubing with a fast flow (1 liter/hr).
8. Allow colorimeter and recorder to warm up for 30 min.
9. Run a baseline with all reagents feeding Type II water through the sample line.

**NOTE:** Use polyethylene tubing for sample line.

**NOTE:** When new tubing is used, about 2 hours may be required to flush residual phenol from the tubing and obtain a stable baseline.

10. Place appropriate standards in the sampler in order of decreasing concentration.
11. Complete loading of the sampler tray with unknown and quality assurance/quality control samples in glass tubes.
12. Run with sensitivity setting at full scale or 500.
13. When the baseline becomes steady, switch sample from Type II water to samples and begin analysis.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit, or of a reagent blank.

The method detection limit for phenolics in aqueous solutions is 50 µg/L.

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 20 percent or less between the measured phenolic concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 15\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

## 9.4 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the instrument detection limit.

## 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 10\%$  of the known concentration.

## 9.6 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - phenolics, to the 500 mL aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted/digested and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 15\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 20\%$ .

## 10.0 Method Performance

In a single laboratory using sewage samples at concentrations of 3.8, 15, 43, and 89  $\mu\text{g/L}$ , the standard deviations were  $\pm 0.5$ , 0.6, 0.6, and 1.0  $\mu\text{g/L}$ , respectively. At concentrations of 73, 146, 299, and 447  $\mu\text{g/L}$ , the standard deviations were  $\pm 1.0$ , 1.8, 4.2, and 5.3  $\mu\text{g/L}$ , respectively.

In a single laboratory using sewage samples at concentrations of 5.3 and 82  $\mu\text{g/L}$ , the recoveries were 78% and 98%, respectively. At concentrations of 168 and 489  $\mu\text{g/L}$ , the recoveries were 97% and 98%, respectively.

## 11.0 Calculations and Reporting

If dilutions were performed, the appropriate factors must be applied to sample values. Compute concentration of samples by comparing sample peak heights with standards. All results should be reported in  $\mu\text{g/L}$  with up to three significant figures.

## 12.0 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. Method 510. 14th Edition, APHA, New York, New York. p. 574.

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

Gales, M.E., and R. L. Booth. 1976. Automated 4-AAP Phenolic Method. AWWA 68:540.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

# TOTAL POLYCHLORINATED BIPHENYLS (PCBs) AND PESTICIDES IN WATERS AND ELUTRIATES

## 1.0 Scope and Application

This method is suitable for the determination of chlorinated pesticides and PCB congeners in waters and elutriates. Table 1 presents the PCB congeners most commonly found in the environment while Table 2 list the pesticides of concern in the Great Lakes. All these compounds may be determined using this method.

This procedure is based on a National Oceanic and Atmospheric Administration (NOAA) method for the determination of Extractable Toxic Organic Compounds in marine sediments (NOAA, 1985) for the quantification and clean-up of the extracts and SW-846 method 8270 (USEPA, 1986) for the extraction of the waters and elutriates.

The extracts produced from this method (sections 8.1 through 8.6) can be used in the determination of PCBs, pesticides, and polynuclear aromatic hydrocarbons (PAHs).

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

The sample is extracted in a separatory funnel with methylene chloride ( $\text{CH}_2\text{Cl}_2$ ). The resultant extract is cleaned-up with silica gel and alumina. Additional clean-up steps to remove biological macromolecules are performed using Sephadex LH-20. PCB congeners and pesticides are then quantified using a glass capillary column to resolve all congeners and gas chromatography/electron capture detector (GC/ECD). The concentrations of 20 congeners (Table 3) will be summed to determine the total PCB content in the sediment.

The same extract used to analyze for PCBs and pesticides can be used to analyze polynuclear aromatic hydrocarbons (PAHs) using gas chromatography/mass spectrometry (GC/MS). The method for PAH determination is provided in this methods manual.

Table 1. PCB Congeners Commonly Identified in the Great Lakes.

BZ#	Structure	BZ#	Structure
1	2-chlorobiphenyl	105	2,3,3',4,4'-pentachlorobiphenyl
3	4-chlorobiphenyl	107	2,3,3',4',5-pentachlorobiphenyl
4	2,2'-dichlorobiphenyl	115	2,3,4,4',6-pentachlorobiphenyl
5	2,3-dichlorobiphenyl	119	2,3',4,4',6-pentachlorobiphenyl
6	2,3'-dichlorobiphenyl	122	2',3,3',4,5-pentachlorobiphenyl
9	2,5-dichlorobiphenyl	123	2',3,4,4',5-pentachlorobiphenyl
12	3,4-dichlorobiphenyl	128	2,2',3,3',4,4'-hexachlorobiphenyl
15	4,4'-dichlorobiphenyl	129	2,2',3,3',4,5-hexachlorobiphenyl
16	2,2',3-trichlorobiphenyl	136	2,2',3,3',6,6'-hexachlorobiphenyl
18	2,2',5-trichlorobiphenyl	137	2,2',3,4,4',5-hexachlorobiphenyl
19	2,2',6-trichlorobiphenyl	138	2,2',3,4,4',5'-hexachlorobiphenyl
22	2,3,4'-trichlorobiphenyl	141	2,2',3,4,5,5'-hexachlorobiphenyl
25	2,3',4-trichlorobiphenyl	149	2,2',3,4',5',6-hexachlorobiphenyl
26	2,3',5-trichlorobiphenyl	151	2,2',3,5,5',6-hexachlorobiphenyl
27	2,3',6-trichlorobiphenyl	153	2,2',4,4',5,5'-hexachlorobiphenyl
28	2,4,4'-trichlorobiphenyl	157	2,3,3',4,4',5'-hexachlorobiphenyl
29	2,4,5-trichlorobiphenyl	158	2,3,3',4,4',6-hexachlorobiphenyl
31	2,4',5-trichlorobiphenyl	167	2,3',4,4',5,5'-hexachlorobiphenyl
37	3,4,4'-trichlorobiphenyl	170	2,2',3,3',4,4',5-heptachlorobiphenyl
40	2,2',3,3'-tetrachlorobiphenyl	171	2,2',3,3',4,4',6-heptachlorobiphenyl
41	2,2',3,4-tetrachlorobiphenyl	177	2,2',3,3',4,5,6-heptachlorobiphenyl
44	2,2',3,5'-tetrachlorobiphenyl	180	2,2',3,4,4',5,5'-heptachlorobiphenyl
47	2,2',4,4'-tetrachlorobiphenyl	183	2,2',3,4,4',5,6-heptachlorobiphenyl
49	2,2',4,5'-tetrachlorobiphenyl	185	2,2',3,4,5,5,6'-heptachlorobiphenyl
52	2,2',5,5'-tetrachlorobiphenyl	187	2,2',3,4',5,5',6-heptachlorobiphenyl
53	2,2',5,6'-tetrachlorobiphenyl	189	2,3,3',4,4',5,5'-heptachlorobiphenyl
56	2,3,3',4'-tetrachlorobiphenyl	190	2,3,3',4,4',5,6-heptachlorobiphenyl
66	2,3,4,4'-tetrachlorobiphenyl	191	2,3,3',4,4',5',6-heptachlorobiphenyl
70	2,3',4',5-tetrachlorobiphenyl	193	2,3,3',4',5,5',6-heptachlorobiphenyl
75	2,4,4',6-tetrachlorobiphenyl	194	2,2',3,3',4,4',5,5'-octachlorobiphenyl
77	3,3',4,4'-tetrachlorobiphenyl	195	2,2',3,3',4,4',5,6-octachlorobiphenyl
82	2,2',3,3',4-pentachlorobiphenyl	196	2,2',3,3',4,4',5',6-octachlorobiphenyl
83	2,2',3,3',5-pentachlorobiphenyl	198	2,2',3,3',4,5,5',6-octachlorobiphenyl
84	2,2',3,3',6-pentachlorobiphenyl	199	2,2',3,3',4,5,6,6'-octachlorobiphenyl
85	2,2',3,4,4'-pentachlorobiphenyl	200	2,2',3,3',4,5',6,6'-octachlorobiphenyl
87	2,2',3,4,5'-pentachlorobiphenyl	201	2,2',3,3',4',5,5',6-octachlorobiphenyl
91	2,2',3,4',6-pentachlorobiphenyl	202	2,2',3,3',5,5',6,6'-octachlorobiphenyl
92	2,2',3,5,5'-pentachlorobiphenyl	205	2,3,3',4,4',5,5',6-octachlorobiphenyl
95	2,2',3,5',6-pentachlorobiphenyl	206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl
97	2,2',3',4,5-pentachlorobiphenyl	207	2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl
99	2,2',4,4',5-pentachlorobiphenyl	208	2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl
101	2,2',4,5,5'-pentachlorobiphenyl		

Table 2. Pesticides of Concern in the Great Lakes.

aldrin	<u>trans</u> -nonachlor
$\alpha$ -chlordane	<u>o,p'</u> -DDE
dieldrin	<u>p,p'</u> -DDE
heptachlor	<u>o,p'</u> -DDD
heptachlor epoxide	<u>p,p'</u> -DDD
hexachlorobenzene	<u>o,p'</u> -DDT
lindane ( $\gamma$ -BHC)	<u>p,p'</u> -DDT
mirex	

Table 3. Twenty PCB Congeners to be Summed to Determine Total PCB Content<sup>a</sup>.

<u>BZ#</u>	<u>Structure</u>	<u>BZ#</u>	<u>Structure</u>
8	2,4'-dichlorobiphenyl	126	3,3',4,4',5-pentachlorobiphenyl
18	2,2',5-trichlorobiphenyl	128	2,2',3,3',4,4'-hexachlorobiphenyl
28	2,4,4'-trichlorobiphenyl	138	2,2',3,4,4',5'-hexachlorobiphenyl
44	2,2',3,5'-tetrachlorobiphenyl	153	2,2',4,4',5,5'-hexachlorobiphenyl
52	2,2',5,5'-tetrachlorobiphenyl	169	3,3',4,4',5,5'-hexachlorobiphenyl
66	2,3,4,4'-tetrachlorobiphenyl	170	2,2',3,3',4,4',5-heptachlorobiphenyl
77	3,3',4,4'-tetrachlorobiphenyl	180	2,2',3,4,4',5,5'-heptachlorobiphenyl
101	2,2',4,5,5'-pentachlorobiphenyl	187	2,2',3,4',5,5',6-heptachlorobiphenyl
105	2,3,3',4,4'-pentachlorobiphenyl	206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl
118	2,3',4,4',5-pentachlorobiphenyl	209	2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl

a = The selected congeners are a combination of those presented in the *Inland Testing Manual* (USEPA/USACE, 1998 and NOAA method (NOAA, 1985).

### 3.0 Interferences

Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large late-eluting peaks. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding

contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.001 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Centrifuge, capable of holding 250 mL centrifuge tubes and maintaining speeds of 1500 rpm.
4. Desiccator and desiccant. Desiccants generally used include: anhydrous calcium sulfate, silica gel, or phosphorus pentoxide. Indicating desiccants are preferable since they show when the desiccant needs to be changed or regenerated.
5. Gas chromatograph (GC) including:
  - a. dual capillary column inlet system,
  - b. autosampler,
  - c. cartridge tape unit, and
  - d. electron capture detector (ECD), two are needed.
6. Modified Kontes tube heater (block contains: Al inserts fitted to the 0.7 mL line of the Kuderna-Danish tube tip and an Al-foil shroud.
7. Molecular sieve traps (for gas cylinder)

**NOTE:** One suggested source for the molecular sieve traps is Hydro-Purge model ASC-I, Coast Engineering Laboratory, Gardena, California.

8. Oxygen traps.
9. UV light source.
10. Water bath, capable of maintaining a temperature of  $80 \pm 2^\circ \text{C}$ .

### 4.2 Materials

1. Beakers, 250 mL, or equivalent.
2. Centrifuge tubes, 250 mL, amber, with Teflon™ caps.
3. Chromatography column with reservoir 250 mL, 19 mm ID, 30 cm.

4. Erlenmeyer flask, 500 mL, with stopper.
5. Erlenmeyer flask, 1 L, with stopper.
6. Funnel, curved-stem (curve must be glassblown).
7. Funnel, 200 mm OD, long-stem.
8. Funnel, powder.
9. GC column, silicon-coated fused silica capillary, DB-5, 30 m x 0.25 mm I.D.
10. GC column, silicon-coated fused silica capillary, DB-17HT, 30 m x 0.25 mm I.D.
11. Graduated cylinder, 500 mL.
12. Graduated cylinder, 100 mL.
13. Graduated cylinder, 50 mL.
14. Kontes concentrator tube, 25 mL, with stopper.
15. Kuderna-Danish concentrator tube, 10 mL, graduated.
16. Kuderna-Danish evaporative flask, 500 mL.
17. pH paper, wide range, capable of determining pH from 4 to 10.
18. Separatory funnel, 2 L, with Teflon™ stopcock.
19. Snyder column, 3-ball macro.
20. Snyder column, 2-ball micro.
21. Syringe, 2000 µL.
22. Syringe, 800 µL.
23. Syringe, 400 µL.
24. Syringe, 200 µL.
25. Syringe, 100 µL.
26. Syringe, 50 µL.
27. Syringe, 10 µL.
28. Teflon wash-bottle, 500 mL (to be filled with CH<sub>2</sub>Cl<sub>2</sub>).
29. Transfer pipets (Pasteur style) with rubber bulbs.
30. GC vials, 2 mL.
31. GC vials, 100 µL, conical.
32. Volumetric flask, class A, 10 mL.
33. Volumetric pipet, 50 mL.

## 5.0 Reagents

1. Alumina, 80-200 mesh. Alumina should be activated at 120° C for 2 hr and then cooled to room temperature in a desiccator just before weighing and use.

2. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
3. Azulene, reagent grade (C<sub>15</sub>H<sub>18</sub>).
4. Helium, grade 4.5 (purified, ≥99.995 %).
5. Hexane, high purity (C<sub>6</sub>H<sub>14</sub>). Each solvent lot should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the solvent has a concentration <MDL, then the solvent can be used.
6. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
7. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
8. Methanol, high purity (CH<sub>3</sub>OH). Each solvent lot should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the solvent has a concentration <MDL, then the solvent can be used.
9. Methylene chloride (dichloromethane), high purity (CH<sub>2</sub>Cl<sub>2</sub>). Each solvent lot should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the solvent has a concentration <MDL, then the solvent can be used.
10. Pentane, high purity (C<sub>5</sub>H<sub>12</sub>). Each solvent lot should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the solvent has a concentration <MDL, then the solvent can be used.
11. Perylene, reagent grade (C<sub>20</sub>H<sub>12</sub>).
12. Sand, Ottawa, MCB, kiln-dried, 30-40 mesh. Sand should be acid-washed (steeped in *aqua regia* (ACS grades HNO<sub>3</sub>:HCl, 1:3, v:v) overnight, then washed three times each with H<sub>2</sub>O, CH<sub>3</sub>OH and CH<sub>2</sub>Cl<sub>2</sub>, dried, and stored at 120° C.
13. Sephadex LH-20, size-exclusion gel. Sephadex LH-20 should be swelled overnight in 6:4:3 solvent.
14. Silica gel, Davison Type 923 or Amicon No. 84080. Silica should be activated at 700° C for 18 hr, stored at 170° C, and cooled to room temperature in a desiccator just before weighing and use.

15. Sodium hydroxide, 10 N (NaOH). Add 20 g of NaOH to 400 mL Type II water. Dilute to 500 mL with Type II water.
16. Sodium sulfate, reagent grade, anhydrous granular (Na<sub>2</sub>SO<sub>4</sub>). Sodium sulfate should be CH<sub>2</sub>Cl<sub>2</sub> washed, dried, stored at 120° C, and cooled to room temperature in a desiccator before weighing and use.
17. PCB/pesticide standard stock solution (100 µg/mL). From commercially available neat PCB and pesticide standards, weigh 1.00 mg of each congener and pesticide and dissolve in 5 mL hexane. Dilute to 10.0 mL with hexane.

**NOTE:** PCB congener standards may also be purchased commercially at concentrations of 100 µg/mL.

18. PCB/pesticide primary dilution standard solution (1 µg/mL). Accurately measure a 100 µL aliquot of the PCB and pesticide standard stock solution and dilute to 10.0 mL of hexane.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the sediments should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

A holding time of 7 days until extraction and 40 days from extraction to analysis is generally cited for this parameter.

Samples should be stored under refrigerated conditions (4° C).

**NOTE:** Samples can be frozen to extend the holding time for up to 1 year.

All sample containers must be prewashed with detergents, acids, and Type II water. Glass containers should be used for the storage of samples to be analyzed for PCBs in waters and elutriates. All glassware and materials contacting the solvents should be washed with CH<sub>2</sub>Cl<sub>2</sub> three times prior to use.

An option to the  $\text{CH}_2\text{Cl}_2$  washing of the glassware is to combust the glassware in a muffle oven at  $400^\circ\text{C}$  for 4 hours.

## 7.0 Calibration and Standardization

### 7.1 General

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^\circ\text{C}$ .

The water bath and Kontes tube heater should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^\circ\text{C}$ .

### 7.2 Sephadex LH-20 Column Calibration

Information on preparing the Sephadex LH-20 column is presented in Attachment A.

1. Add enough azulene (approximately 10 mg/mL) and perylene (approximately 1 mg/mL) to approximately 50 mL of 6:4:3 solvent to produce a deeply colored solution.

**NOTE:** Make sure that the azulene and perylene are completely dissolved.

2. Place a 100 mL cylinder beneath the column and using a transfer pipet, cautiously remove any excess 6:4:3 solvent from the top of the packing.
3. Using a transfer pipet, cautiously apply 2 mL of the azulene/perylene calibration solution onto the column. Use a circular motion to dispense the solution just above the packing, and drip the solution slowly down the column wall so as not to disturb the packing.
4. Open the stopcock, drain to the packing top, and close the stopcock.

5. Add approximately 0.5 mL of solvent to the top of the column. Drain to the packing top, and close the stopcock.
6. Repeat step 5 once.
7. Add 100 mL of solvent, and open the stopcock.
8. Elute the solvent until all of the perylene has emerged, using the UV light to monitor the perylene. Record the volumes at which the azulene and perylene start and finish eluting.
9. If the azulene emerges in the 50-65 mL range, and the perylene emerges in the 60-80 mL range without distinct tailing on the packing, proceed to step 10. Otherwise, recycle the packing (Attachment A).
10. Discard the eluate. Add 50 mL of solvent to the column, and flush the packing by eluting 50 mL into the cylinder. Again, discard the eluate.
11. The column is now ready for the next sample.

**NOTE:** If the column is to be stored, maintain 30-50 mL of solvent in the column reservoir, and cover the top with aluminum foil. Remove the solvent if it separates into 2 phases, add 80 mL of fresh 6:4:3 solvent, and elute 50 mL.

### 7.3 GC Calibration

Calibration standards at a minimum of five concentration levels should be prepared. One of the calibration standards should be at a concentration near, but above, the method detection limit; the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in Tables 2 and 3 may be included). All initial calibration standards should be stored at -10° C to -20° C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The daily calibration standard (ongoing calibration should be prepared weekly and stored at 4° C.

Using the PCB/pesticide primary dilution standard solution, prepare the following suggested standards in 10 mL volumetric flasks:

<u>Primary Dilution Standard Solution (µL)</u>	<u>Concentration (µg/L)</u>
50	5
200	20
400	40
800	80
2000	200

Each standard should be brought to volume with hexane.

Linearity of the GC is determined by calculation of the individual response factors (RF) for each standard concentration using the following formula:

$$\text{RF} = \text{total peak area/mass of injected analyte.}$$

The calibration curve will be considered linear if the %RSD is  $\leq 30\%$  for each compound.

## 8.0 Procedure

### 8.1 Water and Elutriate Extraction

1. Using a 1 liter graduated cylinder, measure 1 liter of sample and transfer to a 2 liter separatory funnel.

**NOTE:** If high concentrations are anticipated, a smaller sample volume may be used and diluted to 1 liter with Type II water.

2. Check the pH of the sample with wide-range pH paper and, if necessary, adjust the pH to greater than 11 with 10 N NaOH.
3. Add 60 mL methylene chloride to the separatory funnel.
4. Add all surrogate spike solutions (see section 9.7).

**NOTE:** Make certain that the solutions are placed into the  $\text{CH}_2\text{Cl}_2$ .

5. Seal and shake the separatory funnel vigorously for 1-2 minutes with periodic venting to release excess pressure.

**NOTE:** Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to prevent unnecessary exposure of the analyst to the organic vapor.

6. Allow the organic layer to separate from the water phase for a minimum of 10 minutes.

**NOTE:** If the emulsion interface between layers is more than one-third the size of the solvent layer, a mechanical technique should be used to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical method.

7. Collect the solvent extract in an Erlenmeyer flask.

**NOTE:** If the emulsion cannot be broken (recovery of <80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and follow procedures given in SW-846 Method 3520 (USEPA, 1986).

8. Repeat steps 4 through 7 two more times using fresh 60 mL portions of methylene chloride.
9. Combine the three extracts.

## 8.2 Extract Concentration

1. Dry the extract by passing it through a drying column containing about 10 cm anhydrous sodium sulfate.
2. Collect the dried extract in a K-D concentrator.
3. Rinse the Erlenmeyer flask, which contained the original solvent extract, with 20-30 mL methylene chloride and add it to the drying column to complete a quantitative transfer of the sample extract.
4. Add one or two clean boiling chips to the evaporation flask.
5. Attach a three-ball Snyder column and prewet the Snyder column by adding approximately 1 mL methylene chloride to the top of the column.

6. Place the K-D apparatus on a hot water bath (80-90° C) so that the concentrator is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor.

**NOTE:** The Snyder column may need to be rewetted with 1 mL of  $\text{CH}_2\text{Cl}_2$  if the extract solution is not boiling when the Snyder column is initially wetted in step 5.

7. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10-20 minutes.

**NOTE:** At the proper rate of distillation, the balls of the chamber will actively chatter but the chambers will not flood. If the chambers flood, lightly tap the Snyder column with a soft blunt object.

8. When the apparent volume of the liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.
9. Remove the Snyder column and rinse both the flask and its lower joints into the concentrator tube with 1-2 mL methylene chloride.
10. Add a clean boiling chip to the concentrator tube.
11. Attach a two-ball micro-Snyder column and prewet the column by adding 0.5 mL methylene chloride to the top of the column.
12. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water.
13. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes.

**NOTE:** At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. If the chambers flood, lightly tap the Snyder column with a soft blunt object.

14. When the apparent volume of extract reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

15. Remove the Snyder column and rinse both the flask and its lower joints into the concentrator tube with 0.2 mL methylene chloride twice.
16. Adjust the final volume to 1.0 mL with methylene chloride.

**NOTE:** If cleanup of the extract will not be performed immediately, stopper the concentrator tube and store under refrigerated conditions (4° C).

**NOTE:** If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon-lined screw cap, and appropriately labeled.

### 8.3 Silica Gel/Alumina Chromatography

**NOTE:** The laboratory temperature must be <80° F (27° C). On warm days proceed more slowly to avoid vapor bubbles.

**NOTE:** Columns should be prepared just prior to use.

1. Add 100 mL of CH<sub>2</sub>Cl<sub>2</sub> and between 5 and 15 mm glass wool plug to a 19 mm ID column with a stopcock. Tamp the plug well to remove any bubbles.
2. Add the 10 g alumina to a beaker and slowly add 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. Gently swirl the beaker for 30 sec, and let it stand for 5 min (to remove all air bubbles).
3. Add the 20 g silica gel to a 2nd beaker. Slowly add 40 mL of CH<sub>2</sub>Cl<sub>2</sub> to the beaker. Gently swirl the beaker for 30 sec, and let it stand for 5 min (to remove all air bubbles).
4. Place a curved-stem funnel into the column reservoir so that the funnel tip hangs well off-center. Swirl the beaker to resuspend the alumina from step 2, and pour the slurry into the column.
5. Wash the beaker with approximately 5 mL of CH<sub>2</sub>Cl<sub>2</sub>, and add the washings to the column. Repeat the wash twice.
6. After the particles settle, open the stopcock for 30 sec to allow the alumina to pack more tightly, then close the stopcock.

**NOTE:** Gentle tapping of the column while the stopcock is open will assist in the settling of the alumina and silica gel.

7. Add the silica gel from step 3 to the column, as in steps 4 and 5.
8. After the particles settle, open the stopcock. While the solvent still drains, add 1 mL of sand through the powder funnel.
9. Drain  $\text{CH}_2\text{Cl}_2$  to the packing top, then close the stopcock.
10. Add 30 mL of 1:1  $\text{CH}_2\text{Cl}_2$ :pentane to the column. Drain to the packing top, then close the stopcock. Discard the eluates.
11. With a transfer pipet, cautiously transfer the extract to the top of the packing. Drain to the packing top, then close the stopcock.
12. Wash down the extract tube with 0.5 mL of 1:1  $\text{CH}_2\text{Cl}_2$ :pentane, and add the washings to the top of the packing. Drain to the packing top, then close the stopcock.
13. Repeat step 12 three times.
14. Add 200 mL of 1:1  $\text{CH}_2\text{Cl}_2$ :pentane, and continue eluting at approximately 3 mL/min.
15. Collect 20 mL of eluate, then close the stopcock, and discard the contents of the cylinder.
16. Replace the cylinder with a labeled flask and collect eluate until the column runs dry.

#### 8.4 Concentration of Extract

1. Add 3-4 boiling chips to the flask from step 15, section 8.3.
2. Attach a Snyder column and concentrate the fraction in a 60° C water bath to 10-15 mL, and transfer it to a concentrator tube.

**NOTE:** It is necessary to wet the Snyder column by adding  $\text{CH}_2\text{Cl}_2$  to the top of the column prior to sample boiling.

3. Wash down the flask with 3-4 mL of  $\text{CH}_2\text{Cl}_2$ , and add the washings to the tube.
4. Repeat step 3 once.
5. Add one boiling chip to the tube and concentrate the fraction to between 0.9 and 1.0 mL.
6. Add 2 mL of hexane to the tube and concentrate to between 0.9 and 1.0 mL.
7. Add approximately 0.7 mL of  $\text{CH}_3\text{OH}$  and 0.5 mL of  $\text{CH}_2\text{Cl}_2$ .

**NOTE:** This step results in a final solution ratio of 6:4:3 hexane: $\text{CH}_3\text{OH}$ : $\text{CH}_2\text{Cl}_2$  (v:v:v).

**NOTE:** The extract must be dissolved in the solvent (no layers), with the total volume  $\leq 2.3$  mL.

## 8.5 Sephadex LH-20 Chromatography

**NOTE:** It is important to check column calibration on a monthly basis.

**NOTE:** During column storage, maintain 30-50 mL of the solvent in the column reservoir and cover the top with aluminum foil to minimize evaporation. If the solvent in the reservoir separates into 2 phases, remove it and replace it with  $>80$  mL of fresh 6:4:3 solvent, then elute 50 mL.

1. Remove the excess solvent from the top of the column using a transfer pipet.
2. Add 10 mL of the 6:4:3 solvent to the column. Drain to the packing top, and close the stopcock. Discard the eluate.
3. Wash the column top with 2 mL of  $\text{CH}_2\text{Cl}_2$ , and place the 50-mL cylinder under the column.
4. Using a transfer pipet, carefully apply the extract from step 7, section 8.4 to the column.
5. Use a circular motion to dispense the sample immediately above the packing, dripping it slowly down the column wall so as not to disturb the packing.
6. Drain to the packing top, and close the stopcock.
7. Wash down the tube with 0.5 mL of 6:4:3 solvent, and apply the washings to the column. Drain to the packing top, and close the stopcock.
8. Repeat step 7 once.
9. Wash down the column wall with approximately 3 mL of 6:4:3 solvent, applied above the base of the reservoir. Drain to the packing top, and close the stopcock.
10. Repeat step 9 once.
11. Cautiously add approximately 150 mL of 6:4:3 solvent to the column without disturbing the packing.
12. Collect 25 mL of eluate in the 50 mL cylinder. Close the stopcock, and discard this eluate.
13. Replace the cylinder with a concentrator tube. Open the stopcock, collect approximately 15 to 20 mL of eluate (the amount calibrated in Section 7.2 steps 8 and 9 from just before

where azulene first emerges from the column), then close the stopcock.

14. Archive this fraction.

**NOTE:** This fraction is archived in case early eluting compounds are not identified in the next fraction. If early eluting compounds are not identified in the next fraction, analyze the archived fraction for these compounds. If the compounds are identified in the archived fraction, a re-calibration of the Sephadex LH-20 column is necessary.

15. Place a 100 mL cylinder under the column. Open the stopcock, and collect approximately 50 to 55 mL of eluate (the amount calibrated in Section 7.2, steps 8 and 9 from 5 mL after the last perylene has eluted). Close the stopcock, and transfer the eluate to a flask.
16. Wash down the cylinder with 3 to 4 mL of  $\text{CH}_2\text{Cl}_2$ , and add the washings to the flask.
17. Repeat step 16 once.
18. Replace the 100 mL cylinder with a waste cylinder, and elute to the top of the packing. Discard this eluate. Add 50 mL of solvent and cap. The column is now ready for the next sample.

## 8.6 Concentration of Sephadex LH-20 Fraction

1. Add 3-4 boiling chips to the flask from step 17 section 8.5, and attach a Snyder column.

**NOTE:** It is necessary to wet the Snyder column by adding  $\text{CH}_2\text{Cl}_2$  to the top of the column prior to sample boiling.

2. Concentrate the fraction in a 75° C water bath to 10-15 mL, and transfer it to a concentrator tube.
3. Wash down the flask with 3-4 mL of  $\text{CH}_2\text{Cl}_2$ , and add the washings to the tube.
4. Repeat step 3 once.
5. Add one boiling chip to the tube and concentrate the fraction to between 0.9 and 1.0 mL.
6. Add 7 mL of hexane to the tube and concentrate to between 0.9 and 1.0 mL.

## 8.7 GC/ECD Analysis

The analyst should follow the instructions provided by the instrument's manufacturer for GC operation and maintenance. The following machine operating conditions are required for the proper determination and separation of the PCB congeners and pesticides:

### Machine Operating Conditions

Helium carrier	1.2 mL/min
Initial oven temperature	100° C
Initial hold time	1 min
First ramp rate	5°/min
First ramp final temperature	140°
Second hold time	1 min
Second ramp rate	1.5°/min
Second ramp final temperature	250° C
Third hold time	1 min
Third ramp rate	10°/min
Final temperature	300° C
Final hold time	5 min
ECD temperature	325° C
Injector port temperature	275° C

The primary quantification column should be a DB-5 0.25 mm ID column with a 30 m length. The secondary confirmation column should be a DB-17HT 0.25 mm ID column with a 30 m length.

When a PCB congener or pesticide is identified on the quantification column, the chromatogram of the confirmation column should also be checked to verify the identification of the analyte. If, however, the area of the confirmation column is lower than that of the quantification column, the area of the analyte in the confirmation column should be used to calculate the concentration of the analyte (along with the areas of the surrogates from the confirmation column).

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit.

The method detection limit for PCBs in water and elutriate matrices is 0.01 µg/L per congener.

The method detection limits for pesticides in water and elutriate matrices are 0.1 µg/L per compound.

**NOTE:** Method detection limits can be lowered by extracting larger amounts of waters or elutriates or by further concentrating the final extract volume (<1 mL).

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 25 percent or less between the measured total PCB or pesticide concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 30\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

## 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 30\%$  of the mean RF from the initial calibration curve.

## 9.6 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - PCBs or pesticides, to the 1 L aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 30\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have a relative percent difference (RPD) of  $\leq 25\%$ .

## 9.7 Surrogate Spikes

A surrogate spike is defined as the addition of an organic compound which is similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in the environmental sample (USEPA, 1986). These compounds are spiked into all blanks, standards, samples, and spiked samples prior to extraction. Surrogate spikes should be spiked at between 50 and 100 times the method detection limit. Surrogate spike recoveries should be  $\pm 30\%$  of the known spiking concentration.

The following surrogate spike compounds are recommended:

- 4,4'-dibromooctafluorobiphenyl (DBOFB)
- decachlorobiphenyl (DCB)
- PCB congener 103
- PCB congener 198

## 9.8 Internal Standards

An internal standard (also known as GC standard) is added immediately prior to analysis by GC (i.e., when loading the GC vials). The compound(s) added are sensitive to the detector and are a measure of analyte recovery without (or with highly reduced) matrix effects. These compounds are spiked into all blanks, standards, samples, and spiked samples. Internal standards should be spiked at between 50 and 100 times the method detection limit. Internal standard recoveries should be  $\pm 30\%$  of the known concentration. The recommended internal standard for this method is tetrachloro-m-xylene (TCMX).

Control charts for the internal standard recoveries, with  $\pm 2$  and  $3\sigma$  values as warning and action limits, respectively, will be required to be created and updated after each day of analysis to control any systematic bias that may be adding to the overall measurement uncertainty for a given parameter. A value outside the control limits is considered unacceptable, hence, the instrument should be recalibrated and the samples in that batch should be reanalyzed. If bias for a given analysis is indicated, i.e., at least seven successive points occurring on one side of the cumulative means, sample analysis should cease until an explanation is found and the system is brought under control.

## 10.0 Method Performance

Precision and accuracy information are not available at this time.

## 11.0 Calculations and Reporting

Identify the analyte peaks in the chromatograms of the extract fractions by comparing them with the analyte retention times obtained from the chromatogram of the ongoing calibration standard.

**NOTE:** When a PCB congener or pesticide is identified on the quantification column, the chromatogram of the confirmation column should also be checked to verify the identification of the analyte. If, however, the area of the confirmation column is lower than that of the quantification column, the area of the analyte in the confirmation column should be used to calculate the concentration of the analyte (along with the areas of the surrogates from the confirmation column).

The concentration of an analyte in the sediment sample, dry weight basis:

$$\text{PCB/pesticide, } \eta\text{g/L} = \frac{R_1 \times R_2 \times SS}{R_3 \times V_w}$$

where:

$$R_1 = \frac{\text{analyte peak area from the sample}}{\text{surrogate spike peak area from the sample}}$$

$$R_2 = \frac{\text{analyte concentration in the ongoing calibration standard } (\eta\text{g}/\mu\text{L})}{\text{surrogate spike concentration in the ongoing calibration standard } (\eta\text{g}/\mu\text{L})}$$

$$R_3 = \frac{\text{analyte peak area from the ongoing calibration standard}}{\text{surrogate spike peak area from the ongoing calibration standard}}$$

SS = surrogate spike concentration added to sample ( $\eta\text{g}$ )

$V_s$  = volume of water or elutriate extracted (L).

The concentration of the total PCBs in the sediment sample is calculated by summation of the 20 congeners (Table 3) as follows:

$$\text{Total PCBs, } \eta\text{g/L} = \Sigma \text{ congener concentrations}$$

**If the congener concentration is < method detection limit, then a "0" value should be used during summation (i.e., do not add the method detection limit for non-identified congeners).**

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## Attachment A - Sephadex LH-20 Column Packing and Recycling

### A.1 Column Packing

1. Fit a 19 mm ID column with a stopcock, add 10 mL of 6:4:3 solvent and between 5 and 10 mm glass wool plug. Tamp the plug to remove any air bubbles.
2. Add approximately 1 mL of sand to the column, and tap the column gently so that the sand forms a smooth layer on top of the glass wool.
3. Pour the swelled Sephadex gel through the funnel into the column until the gel fills the column and about 1/4 of the reservoir.
4. Allow 10 min for the Sephadex to settle. Open the stopcock, and elute 80 mL of solvent to ensure firm packing. Add more solvent as needed. Leave 30 mL of solvent in the column reservoir. Cover the top with aluminum foil, and allow the packing to settle overnight.
5. Open the stopcock, and elute 10 mL of solvent, then close the stopcock. Remove the excess Sephadex packing from the top with a transfer pipet until the height of the Sephadex is 26.5 cm.
6. Gently add approximately 1 mL of sand onto the packing so that it forms an even layer on the top. (The column may be tapped or tilted slightly to get an even layer of sand.)
7. Examine the packing for air bubbles. If bubbles are evident, elute approximately 250 mL of warm (about 35° C) solvent through the column. If the bubbles persist, recycle the packing (see section A.2).

### A.2 Recycling Sephadex LH-20 Column Packing

**NOTE:** When the column no longer maintains its calibration with azulene/perylene, recycle the packing.

1. Decant any solvent in the column reservoir.
2. Empty the column packing into a beaker 4 times the volume of the packing.
3. Wash with  $\text{CH}_2\text{Cl}_2$ .
4. Add enough  $\text{CH}_2\text{Cl}_2$  to float Sephadex particles in the upper half of the beaker.
5. Remove all glass wool with forceps (mandatory).
6. Cover the beaker and let stand for 1 to 2 hours.
7. Decant the floating particles leaving the sand in the beaker.
8. Aspirate the  $\text{CH}_2\text{Cl}_2$  from the Sephadex particles and set them aside.
9. Swell these particles overnight in 6:4:3 solvent before reusing.

# POLYNUCLEAR AROMATIC HYDROCARBONS IN WATERS AND ELUTRIATES (GC/MS, CAPILLARY COLUMN)

## 1.0 Scope and Application

This method is appropriate for the determination of polynuclear aromatic hydrocarbons (PAHs) in water and elutriate samples. Individual polynuclear aromatic compounds that are soluble in methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) and capable of being eluted without derivitization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone are listed in Table 1.

This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

Extraction and quantification techniques are based on SW-846 Method 8270 (USEPA, 1986). The extract clean-up procedures are based on a National Oceanic and Atmospheric Administration (NOAA) method for the determination of Extractable Toxic Organic Compounds in marine sediments (NOAA, 1985).

The extracts produced from this method (sections 8.1 through 8.6) can be used in the determination of polychlorinated biphenyls (PCBs), pesticides, and PAHs.

**NOTE:** The methods presented in this appendix have been prepared to analyze "clean" waters and elutriates. These methods are not intended for use on highly contaminated waters, elutriates, or sediments.

## 2.0 Summary of Method

A measured volume of sample, 1 liter, is serially extracted with methylene chloride in a separatory funnel. The resultant extract is cleaned-up with silica gel and alumina. Additional clean-up steps to remove biological macromolecules are performed using Sephadex LH-20. The final sample extract is injected into a gas chromatograph/mass spectrometer system using a

capillary column for separation, identification, and quantification of the individual PAHs present in the sample.

The same extract used to analyze for PAHs can be used to analyze for PCBs and pesticides using gas chromatography with electron capture detection (GC/ECD). The method for PCB and pesticide determination is provided in this methods manual.

### 3.0 Interferences

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences during the analysis of samples. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing reagent blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

## 4.0 Apparatus and Materials

### 4.1 Apparatus

1. Analytical balance, capable of weighing to 0.001 g.
2. Analytical balance calibration weights, Class S, 3-5 weights covering expected weight range.
3. Centrifuge, capable of holding 250 mL centrifuge tubes and maintaining speeds of 1500 rpm.
4. Desiccator and desiccant. Desiccants generally used include: anhydrous calcium sulfate, silica gel, or phosphorus pentoxide. Indicating desiccants are preferable since they show when the desiccant needs to be changed or regenerated.
5. Gas chromatograph/mass spectrometer system with:
  - a. gas chromatograph system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes,

- analytical columns, and gases. The capillary column should be directly coupled to the source.
- b. mass spectrometer capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode.
  - c. GC/MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used.
  - d. data system: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should also be available.
6. Modified Kontes tube heater (block contains: Al inserts fitted to the 0.7 mL line of the tube tip and an Al-foil shroud).
  7. Molecular sieve traps (for gas cylinder)

**NOTE:** One suggested source for the molecular sieve traps is Hydro-Purge model ASC-I, Coast Engineering Laboratory, Gardena, California.

8. Oxygen traps.
9. UV light source.
10. Water bath, capable of maintaining a temperature of  $80 \pm 2^\circ \text{C}$ .

**NOTE:** The bath should be used in a hood.

## 4.2 Materials

1. Beakers, 250 mL, or equivalent.
2. Centrifuge tubes, 250 mL, amber, with Teflon™ caps.

3. Chromatography column with reservoir 250 mL, 19 mm ID, 30 cm.
4. Erlenmeyer flask, 500 mL, with stopper.
5. Erlenmeyer flask, 1 L, with stopper.
6. Funnel, curved-stem (curve must be glassblown).
7. Funnel, 200 mm OD, long-stem.
8. Funnel, powder.
9. GC column, silicon-coated fused-silica capillary column, DB-5, 30 m x 0.25 mm I.D. (or 0.32 mm I.D.).
10. Graduated cylinder, 500 mL.
11. Graduated cylinder, 100 mL.
12. Graduated cylinder, 50 mL.
13. Kontes concentrator tube, 25 mL, with stopper.
14. Kuderna-Danish concentrator tube, 10 mL, graduated.
15. Kuderna-Danish evaporative flask, 500 mL.
16. pH paper, wide range, capable of determining pH from 4 to 10.
17. Separatory funnel, 2 L, with Teflon™ stopcock.
18. Snyder column, 3-ball macro.
19. Snyder column, 2-ball micro.
20. Syringe, 2000 µL.
21. Syringe, 800 µL.
22. Syringe, 400 µL.
23. Syringe, 200 µL.
24. Syringe, 100 µL.
25. Syringe, 50 µL.
26. Syringe, 10 µL.
27. Teflon wash-bottle, 500 mL (to be filled with CH<sub>2</sub>Cl<sub>2</sub>).
28. Transfer pipets (Pasteur style) with rubber bulbs.
29. GC vials, 2 mL.
30. GC vials, 100 µL, conical.
31. Volumetric flask, class A, 100 mL
32. Volumetric flask, class A, 50 mL
33. Volumetric flask, class A, 10 mL
34. Volumetric pipet, 50 mL.

## 5.0 Reagents

1. Alumina, 80-200 mesh. Alumina should be activated at 120° C for 2 hr and then cooled to room temperature in a desiccator just before weighing and use.

2. ASTM Type II water (ASTM D1193). Water should be continually monitored for the presence of contaminants to verify that they are not present at levels that will interfere with method performance.
3. Azulene, reagent grade (C<sub>15</sub>H<sub>18</sub>).
4. Copper, reagent grade, fine granular. Copper should be activated < 1 hr before use. To activate copper, cover with concentrated HCl and stir with a glass rod. Allow to stand for 5 min followed by washing twice with CH<sub>3</sub>OH and then 3 times with CH<sub>2</sub>Cl<sub>2</sub>. Leave copper covered with CH<sub>2</sub>Cl<sub>2</sub> to avoid contact with air.
5. Helium, grade 4.5 (purified, ≥99.995 %).
6. Hexane, high purity (C<sub>6</sub>H<sub>14</sub>). Each solvent lot should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the solvent has a concentration <MDL, then the solvent can be used.
7. Concentrated hydrochloric acid, reagent grade (HCl). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
8. Concentrated nitric acid, reagent grade (HNO<sub>3</sub>). Acid should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the acid has a concentration <MDL, then the acid can be used.
9. Methanol, high purity (CH<sub>3</sub>OH). Each solvent lot should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the solvent has a concentration <MDL, then the solvent can be used.
10. Methylene chloride (dichloromethane), high purity (CH<sub>2</sub>Cl<sub>2</sub>). Each solvent lot should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the solvent has a concentration <MDL, then the solvent can be used.
11. Pentane, high purity (C<sub>5</sub>H<sub>12</sub>). Each solvent lot should be analyzed to verify that contaminants are not present at levels that will interfere with method performance. If a method blank using the solvent has a concentration <MDL, then the solvent can be used.
12. Perylene, reagent grade (C<sub>20</sub>H<sub>12</sub>).
13. Sand, Ottawa, MCB, kiln-dried, 30-40 mesh. Sand should be acid-washed (steeped in *aqua regia* (ACS grades HNO<sub>3</sub>:HCl, 1:3, v:v) overnight, then washed three times each with Type II H<sub>2</sub>O, CH<sub>3</sub>OH and CH<sub>2</sub>Cl<sub>2</sub>, dried, and stored at 120° C.

14. Sephadex LH-20, size-exclusion gel. Sephadex LH-20 should be swelled overnight in 6:4:3 solvent.
15. Silica gel, Davison Type 923 or Amicon No. 84080. Silica should be activated at 700° C for 18 hr, stored at 170° C, and cooled to room temperature in a desiccator just before weighing and use.
16. Sodium hydroxide, 10 N (NaOH). Add 20 g of NaOH to 400 mL Type II water. Dilute to 500 mL with Type II water.
17. Sodium sulfate, reagent grade, anhydrous granular (Na<sub>2</sub>SO<sub>4</sub>). Sodium sulfate should be CH<sub>2</sub>Cl<sub>2</sub> washed, dried, stored at 120° C, and cooled to room temperature in a desiccator before weighing and use.
18. PAH standard stock solution (1.00 µg/µL). PAH stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

**NOTE:** Prepare stock standard solutions by accurately weighing 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4° C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

Stock standard solutions must be replaced after 1 yr, or sooner, if comparison with quality control check samples indicates a problem.

19. GC/MS tuning standard. A methylene chloride solution containing 50 ng/µL of decafluorotriphenylphosphine (DFTPP) should be prepared. Store at 4° C or less when not being used.

## 6.0 Sample Collection, Preservation, and Handling

Sample collection procedures for the aqueous and sediment samples should be described in the approved sampling manual. Further information on bulk sediment collection procedures may be found in the sampling chapter. Aliquoting procedures from the bulk sediment sample are described in the General Laboratory Practices chapter.

Sample containers should be filled with care so as to prevent contamination due to any portion of the collected sample coming in contact with the sampler's gloves.

Samples should not be collected or stored in the presence of exhaust fumes.

A holding time of 7 days until extraction and 40 days from extraction to analysis is generally cited for this parameter.

The sample should be stored under refrigerated conditions (4° C) in the dark.

All sample containers must be prewashed with detergents, acids, and Type II water. Glass containers should be used for the storage of samples to be analyzed for PAHs in waters and elutriates. All glassware and materials contacting the solvents should be washed with CH<sub>2</sub>Cl<sub>2</sub> three times prior to use.

An option to the CH<sub>2</sub>Cl<sub>2</sub> washing of the glassware is to combust the glassware in a muffle oven at 400° C for 4 hours.

## 7.0 Calibration and Standardization

### 7.1 General

The calibration of the analytical balance is described in the General Laboratory Practices chapter. Additionally, the balance should be checked and cleaned by the manufacturer on a semi-annual or annual basis.

The thermometers should be checked periodically against a NIST certified thermometer to ensure that they are measuring temperature accurately. Thermometers should be accurate within  $\pm 0.5^\circ \text{C}$ .

The water bath and Kontes tube heater should be monitored to ensure that temperature fluctuations do not exceed  $\pm 2^\circ \text{C}$ .

## 7.2 Sephadex LH-20 Column Calibration

Information on preparing the Sephadex LH-20 column is presented in Attachment A.

1. Add enough azulene (approximately 10 mg/mL) and perylene (approximately 1 mg/mL) to approximately 50 mL of 6:4:3 solvent to produce a deeply colored solution.

**NOTE:** Make sure that the azulene and perylene are completely dissolved.

2. Place a 100 mL cylinder beneath the column and using a transfer pipet, cautiously remove any excess 6:4:3 solvent from the top of the packing.
3. Using a transfer pipet, cautiously apply 2 mL of the azulene/perylene calibration solution onto the column. Use a circular motion to dispense the solution just above the packing, and drip the solution slowly down the column wall so as not to disturb the packing.
4. Open the stopcock, drain to the packing top, and close the stopcock.
5. Add approximately 0.5 mL of solvent to the top of the column. Drain to the packing top, and close the stopcock.
6. Repeat step 5 once.
7. Add 100 mL of solvent, and open the stopcock.
8. Elute the solvent until all of the perylene has emerged, using the UV light to monitor the perylene. Record the volumes at which the azulene and perylene start and finish eluting.
9. If the azulene emerges in the 50-65 mL range, and the perylene emerges in the 60-80 mL range without distinct tailing on the packing, proceed to step 10. Otherwise, recycle the packing (Attachment A).
10. Discard the eluate. Add 50 mL of solvent to the column, and flush the packing by eluting 50 mL into the cylinder. Again, discard the eluate.
11. The column is now ready for the next sample.

**NOTE:** If the column is to be stored, maintain 30-50 mL of solvent in the column reservoir, and cover the top with aluminum foil. Remove the solvent if it separates into 2 phases, add 80 mL of fresh 6:4:3 solvent, and elute 50 mL.

### 7.3 GC Calibration

Calibration standards at a minimum of five concentration levels should be prepared. One of the calibration standards should be at a concentration near, but above, the method detection limit; the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method. All initial calibration standards should be stored at -10° to -20° C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The daily calibration standard (ongoing calibration standard) should be prepared weekly and stored at 4° C.

Each GC/MS system must be hardware-tuned to meet the criteria in Table 2 for the GC/MS tuning standard. Analyses should not begin until all these criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. If chromatogram peak degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6 to 12 in. of the capillary column.

Analyze each calibration standard (1 µL containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (Table 1). Calculate response factors (RFs) for each compound as follows:

$$RF = (A_x C_{is}) / (A_{is} C_x)$$

where:

$A_x$  = area of the characteristic ion for the compound being measured.

$A_{is}$  = area of the characteristic ion for the specific internal standard.

$C_x$  = concentration of the compound being measured (ng/µL).

$C_{is}$  = concentration of the specific internal standard (ng/µL).

The average RF should be calculated for each compound. The percent relative standard deviation (%RSD) should also be calculated for each compound. The %RSD should be less than 30% for each compound. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units.

**NOTE:** Late eluting compounds usually have much better agreement.

## 8.0 Procedure

### 8.1 Water and Elutriate Extraction

1. Using a 1 liter graduated cylinder, measure 1 liter of sample and transfer to a 2 liter separatory funnel.

**NOTE:** If high concentrations are anticipated, a smaller sample volume may be used and diluted to 1 liter with Type II water.

3. Check the pH of the sample with wide-range pH paper and, if necessary, adjust the pH to greater than 11 with 10 N NaOH.
4. Add 60 mL methylene chloride to the separatory funnel.

**NOTE:** Be sure to add all surrogate spike solutions at this point. Make certain that the solutions are placed into the  $\text{CH}_2\text{Cl}_2$ .

5. Seal and shake the separatory funnel vigorously for 1-2 minutes with periodic venting to release excess pressure.

**NOTE:** Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to prevent unnecessary exposure of the analyst to the organic vapor.

6. Allow the organic layer to separate from the water phase for a minimum of 10 minutes.

**NOTE:** If the emulsion interface between layers is more than one-third the size of the solvent layer, a mechanical technique should be used to complete the phase separation. The

optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical method.

7. Collect the solvent extract in an Erlenmeyer flask.

**NOTE:** If the emulsion cannot be broken (recovery of <80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and follow procedures given in SW-846 Method 3520 (USEPA, 1986).

8. Repeat steps 4 through 7 two more times using fresh 60 mL portions of methylene chloride.
9. Combine the three extracts.

## 8.2 Extract Concentration

1. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask.
2. Dry the extract by passing it through a drying column containing about 10 cm anhydrous sodium sulfate.
3. Collect the dried extract in a K-D concentrator.
4. Rinse the Erlenmeyer flask, which contained the original solvent extract, with 20-30 mL methylene chloride and add it to the column to complete a quantitative transfer of the sample extract.
5. Add one or two clean boiling chips to the evaporation flask.
6. Attach a three-ball Snyder column and prewet the Snyder column by adding approximately 1 mL methylene chloride to the top of the column.
7. Place the K-D apparatus on a hot water bath (80-90° C) so that the concentrator is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor.
8. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10-20 minutes.

**NOTE:** At the proper rate of distillation, the balls of the chamber will actively chatter but the chambers will not flood.

9. When the apparent volume of the liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.
10. Remove the Snyder column and rinse both the flask and its lower joints into the concentrator tube with 1-2 mL methylene chloride.
11. Add a clean boiling chip to the concentrator tube.
12. Attach a two-ball micro-Snyder column and prewet the column by adding 0.5 mL methylene chloride to the top of the column.
13. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water.
14. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes.

**NOTE:** At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

15. When the apparent volume of extract reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.
16. Remove the Snyder column and rinse both the flask and its lower joints into the concentrator tube with 0.2 mL methylene chloride.
17. Adjust the final volume to 1.0 mL with methylene chloride.

**NOTE:** If analysis of the extract will not be performed immediately, stopper the concentrator tube and store under refrigerated conditions (4° C).

**NOTE:** If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon-lined screw cap, and appropriately labeled.

### 8.3 Silica Gel/Alumina Chromatography

**NOTE:** The laboratory temperature must be <80° F (27° C). On warm days proceed more slowly to avoid vapor bubbles.

**NOTE:** Columns should be prepared just prior to use.

1. Add 100 mL of  $\text{CH}_2\text{Cl}_2$  and between 5 and 15 mm glass wool plug to a 19 mm ID column with a stopcock. Tamp the plug well to remove any bubbles.
2. Add the 10 g alumina to a beaker and slowly add 20 mL of  $\text{CH}_2\text{Cl}_2$ . Gently swirl the beaker for 30 sec, and let it stand for 5 min (to remove all air bubbles).
3. Add the 20 g silica gel to a 2nd beaker. Slowly add 40 mL of  $\text{CH}_2\text{Cl}_2$  to the beaker. Gently swirl the beaker for 30 sec, and let it stand for 5 min (to remove all air bubbles).
4. Place a curved-stem funnel into the column reservoir so that the funnel tip hangs well off-center. Swirl the beaker to resuspend the alumina from step 2, and pour the slurry into the column.
5. Wash the beaker with approximately 5 mL of  $\text{CH}_2\text{Cl}_2$ , and add the washings to the column. Repeat the wash twice.
6. After the particles settle, open the stopcock for 30 sec to allow the alumina to pack more tightly, then close the stopcock.

**NOTE:** Gentle tapping of the column while the stopcock is open will assist in the settling of the alumina and silica gel.

7. Add the silica gel from step 3 to the column, as in steps 4 and 5.
8. After the particles settle, open the stopcock. While the solvent still drains, add 1 mL of sand through the powder funnel.
9. Drain  $\text{CH}_2\text{Cl}_2$  to the packing top, then close the stopcock.
10. Add 30 mL of 1:1  $\text{CH}_2\text{Cl}_2$ :pentane to the column. Drain to the packing top, then close the stopcock. Discard the eluates.
11. With a transfer pipet, cautiously transfer the extract to the top of the packing. Drain to the packing top, then close the stopcock.
12. Wash down the extract tube with 0.5 mL of 1:1  $\text{CH}_2\text{Cl}_2$ :pentane, and add the washings to the top of the packing. Drain to the packing top, then close the stopcock.
13. Repeat step 12 three times.
14. Add 200 mL of 1:1  $\text{CH}_2\text{Cl}_2$ :pentane, and continue eluting at approximately 3 mL/min.
15. Collect 20 mL of eluate, then close the stopcock, and discard the contents of the cylinder.
16. Replace the cylinder with a labeled flask and collect eluate until the column runs dry.

#### 8.4 Concentration of Extract

1. Add 3-4 boiling chips and a few grains of activated copper to the flask from step 15, section 8.3 until no further discoloring of the copper occurs.

**NOTE:** Activated copper is added to the flask to remove elemental sulfur, a potential interferant for GC/ECD analyses.

2. Attach a Snyder column and concentrate the fraction in a 60° C water bath to 10-15 mL, and transfer it to a concentrator tube.

**NOTE:** It is necessary to wet the Snyder column by adding CH<sub>2</sub>Cl<sub>2</sub> to the top of the column prior to sample boiling.

3. Wash down the flask with 3-4 mL of CH<sub>2</sub>Cl<sub>2</sub>, and add the washings to the tube.
4. Repeat step 3 once.
5. Add one boiling chip to the tube and concentrate the fraction to between 0.9 and 1.0 mL.
6. Add 2 mL of hexane to the tube and concentrate to between 0.9 and 1.0 mL.
7. Add approximately 0.7 mL of CH<sub>3</sub>OH and 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub>.

**NOTE:** This step results in a final solution ratio of 6:4:3 hexane:CH<sub>3</sub>OH:CH<sub>2</sub>Cl<sub>2</sub> (v:v:v).

**NOTE:** The extract must be dissolved in the solvent (no layers), with the total volume ≤ 2.3 mL.

## 8.5 Sephadex LH-20 Chromatography

**NOTE:** It is important to check column calibration on a monthly basis.

**NOTE:** During column storage, maintain 30-50 mL of the solvent in the column reservoir and cover the top with aluminum foil to minimize evaporation. If the solvent in the reservoir separates into 2 phases, remove it and replace it with >80 mL of fresh 6:4:3 solvent, then elute 50 mL.

1. Remove the excess solvent from the top of the column using a transfer pipet.

2. Add 10 mL of the 6:4:3 solvent to the column. Drain to the packing top, and close the stopcock. Discard the eluate.
3. Wash the column top with 2 mL of  $\text{CH}_2\text{Cl}_2$ , and place the 50-mL cylinder under the column.
4. Using a transfer pipet, carefully apply the extract from step 7, section 8.4, to the column.
5. Use a circular motion to dispense the sample immediately above the packing, dripping it slowly down the column wall so as not to disturb the packing.
6. Drain to the packing top, and close the stopcock.
7. Wash down the tube with 0.5 mL of 6:4:3 solvent, and apply the washings to the column. Drain to the packing top, and close the stopcock.
8. Repeat step 7 once.
9. Wash down the column wall with approximately 3 mL of 6:4:3 solvent, applied above the base of the reservoir. Drain to the packing top, and close the stopcock.
10. Repeat step 9 once.
11. Cautiously add approximately 150 mL of 6:4:3 solvent to the column without disturbing the packing.
12. Collect 25 mL of eluate in the 50 mL cylinder. Close the stopcock, and discard this eluate.
13. Replace the cylinder with a concentrator tube. Open the stopcock, collect approximately 15 to 20 mL of eluate (the amount calibrated in Section 7.2 steps 8 and 9 from just before where azulene first emerges from the column), then close the stopcock.
14. Archive this fraction.

**NOTE:** This fraction is archived in case early eluting compounds are not identified in the next fraction. If early eluting compounds are not identified in the next fraction, analyze the archived fraction for these compounds. If the compounds are identified in the archived fraction, a re-calibration of the Sephadex LH-20 column is necessary.

15. Place a 100 mL cylinder under the column. Open the stopcock, and collect approximately 50 to 55 mL of eluate (the amount calibrated in Section 7.2, steps 8 and 9 from 5 mL after the last perylene has eluted). Close the stopcock, and transfer the eluate to a flask.

16. Wash down the cylinder with 3 to 4 mL of CH<sub>2</sub>Cl<sub>2</sub>, and add the washings to the flask.
17. Repeat step 16 once.
18. Replace the 100 mL cylinder with a waste cylinder, and elute to the top of the packing. Discard this eluate. Add 50 mL of solvent and cap. The column is now ready for the next sample.

## 8.6 Concentration of Sephadex LH-20 Fraction

1. Add 3-4 boiling chips to the flask from step 17 section 8.5, and attach a Snyder column.

**NOTE:** It is necessary to wet the Snyder column by adding CH<sub>2</sub>Cl<sub>2</sub> to the top of the column prior to sample boiling.

2. Concentrate the fraction in a 75° C water bath to 10-15 mL, and transfer it to a concentrator tube.
3. Wash down the flask with 3-4 mL of CH<sub>2</sub>Cl<sub>2</sub>, and add the washings to the tube.
4. Repeat step 3 once.
5. Add one boiling chip to the tube and concentrate the fraction to between 0.9 and 1.0 mL.
6. Add 7 mL of hexane to the tube and concentrate to between 0.9 and 1.0 mL.

## 8.7 GC/MS Analysis

The analyst should follow the instructions provided by the instrument's manufacturer for GC operation and maintenance. The recommended GC/MS operating conditions for PAH quantification are:

Mass Range	35-500 amu
Scan time	1 sec/scan
Initial column temperature	40° C
Initial hold time:	4 min
Column temperature program	40-270° C at 10° C/min
Final column temperature hold	270° C (until benzo[g,h,i]perylene has eluted)
Injector temperature	250-300° C
Transfer line temperature	250-300° C

Source temperature	According to manufacturer's specifications
Injector	Grob-type, splitless
Sample volume	1-2 $\mu\text{L}$
Carrier gas	Helium at 30 cm/sec.

The primary quantification column should be a DB-5 0.25 mm I.D. column with a 30 m length.

The volume to be injected should ideally contain 100 ng of the PAHs (for a 1  $\mu\text{L}$  injection).

**NOTE:** It is highly recommended that the extract be screened on a GC with flame ionization detection (FID) or GC with photoionization detection (PID) using the same type of capillary column (DB-5 0.25 mm I.D. with a 30 m length). This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

## 9.0 Quality Control

### 9.1 Detection Limits

The method detection limit is defined as 3 times the standard deviation of a minimum of seven replicates of a low level standard whose concentration is within a factor of 10 of the estimated method detection limit.

The method detection limit for PAHs in water and elutriate matrices is 10  $\mu\text{g/L}$ .

**NOTE:** Method detection limits can be lowered by extracting larger amounts of waters or elutriates or by further concentrating the final extract volume (<1 mL).

### 9.2 Replicate Samples

A minimum of one sample from each sample batch should be analyzed in duplicate. The relative percent difference (RPD) should be 25 percent or less between the measured PAH concentrations.

### 9.3 Standard Reference Materials

Standard reference materials, such as NIST standards, should be run to monitor the performance and assess the accuracy/bias of the measurement system. Standard reference materials should be run at a frequency of one per analytical sample batch. The acceptance criterion for the standard reference materials should be  $\pm 30\%$  of the known value or within the certified value provided by the supplier, whichever is larger.

### 9.4 Blanks

A minimum of one reagent blank per sample batch should be analyzed to determine if contamination or any memory effects are occurring. The measured concentration in the reagent blank should be less than or equal to the method detection limit.

One reagent blank should also be analyzed prior to any routine sample analyses to ensure interferences and contamination are under control.

### 9.5 Ongoing Calibration

The calibration of the instrument should be verified by analyzing an independently prepared ongoing check standard every 10 samples. The ongoing calibration check sample should be a mid-calibration range standard prepared from an independent stock solution. The acceptance criterion for the ongoing calibration check sample should be  $\pm 30\%$  of the mean RF from the initial calibration curve.

### 9.6 Matrix Spikes/Matrix Spike Duplicates

A matrix spike/matrix spike duplicate is a sample prepared by adding a known quantity of a target analyte, in this case - PAHs, to the 1 L aliquot of a routine sample for which an independent estimate of the target analyte concentration is available. The concentration of the matrix spike should be at the regulatory standard level or at approximately 10 times the estimated or actual method detection limit. The spiked sample is then extracted and analyzed in the same manner as any other routine sample. Matrix spike recoveries should be within  $\pm 30\%$  of the known spike concentration. Precision between the matrix spike and its duplicate should have an relative percent difference (RPD) of  $\leq 30\%$ .

## 9.7 Surrogate Spikes

A surrogate spike is defined as the addition of an organic compound which is similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in the environmental sample (USEPA, 1986). These compounds are spiked into all blanks, standards, samples, and spiked samples prior to extraction. Surrogate spikes should be spiked at between 50 and 100 times the method detection limit. Surrogate spike recoveries should be  $\pm 30\%$  of the known spiking concentration.

The following surrogate spike compounds are recommended:

naphthalene-d<sub>8</sub>  
acenaphthene-d<sub>10</sub>  
perylene-d<sub>12</sub>

Other surrogate spike compounds that are also commonly used are phenanthrene-d<sub>10</sub> and chrysene-d<sub>12</sub>.

Control charts for the surrogate spikes, with  $\pm 2$  and  $3 \sigma$  values as warning and action limits, respectively, will be required to be created and updated after each day of analysis to control any systematic bias that may be adding to the overall measurement uncertainty for a given parameter. A value outside the control limits is considered unacceptable, hence, the instrument should be recalibrated and the samples in that batch should be reanalyzed. If bias for a given analysis is indicated, i.e., at least seven successive points occurring on one side of the cumulative means, sample analysis should cease until an explanation is found and the system is brought under control.

## 9.8 Internal Standards

An internal standard (also known as GC standard) is added immediately prior to analysis by GC. The compound(s) added are sensitive to the detector and are a measure of analyte recovery without (or with highly reduced) matrix effects. These compounds are spiked into all blanks, standards, samples, and spiked samples. Internal standards should be spiked at between 50 and 100 times the method detection limit. Internal standard recoveries should be  $\pm 30\%$  of the known concentration. The recommended internal standard for this method is tetrachloro-m-xylene (TCMX). An alternate internal standard often used is hexamethylbenzene (HMB).

Control charts for the internal standards, with  $\pm 2$  and  $3\sigma$  values as warning and action limits, respectively, will be required to be created and updated after each day of analysis to control any systematic bias that may be adding to the overall measurement uncertainty for a given parameter. A value outside the control limits is considered unacceptable, hence, the instrument should be recalibrated and the samples in that batch should be reanalyzed. If bias for a given analysis is indicated, i.e., at least seven successive points occurring on one side of the cumulative means, sample analysis should cease until an explanation is found and the system is brought under control.

### 9.9 Ongoing GC/MS Tuning Standard

A 50 ng injection of the GC/MS tuning standard (DFTPP) must be made during each 12 hour shift. Acceptance criteria in the mass spectrum for DFTPP must meet the criteria given in Table 2.

## 10.0 Method Performance

Precision and accuracy information are not available at this time.

## 11.0 Calculations and Reporting

### 11.1 Qualitative Analysis

An analyte is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for the standard reference should be obtained on the GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

The sample component RRT must compare within  $\pm 0.06$  RRT units of the RRT of the standard component. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum. The relative intensities of ions must agree within plus or minus 20% between the standard and sample spectra (i.e., an ion with an abundance of 50% in the standard spectra must have the corresponding sample abundance between 30 and 70 percent).

For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Computer-generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

1. Relative intensities of major ions in the reference spectrum (ion >10% of the most abundant ion) should be present in the sample spectrum.
2. The relative intensities of the major ions should agree within  $\pm 20\%$ . (i.e., an ion with an abundance of 50% in the standard spectrum must have the corresponding sample ion abundance between 30 and 70%).
3. Molecular ions present in the reference spectrum should be present in sample the spectrum.
4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

## 11.2 Quantitative Analysis

When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte.

Calculate the concentration of each identified analyte in the sample as follows:

$$\text{PAH, } \mu\text{g/L} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_o)(V_i)}$$

where:

$A_x$  = area of characteristic ion for compound being measured.

$I_s$  = amount of internal standard injected ( $\eta\text{g}$ ).

$V_t$  = volume of total extract ( $\mu\text{L}$ ).

$A_{is}$  = area of characteristic ion for the internal standard.

$R_F$  = response factor for compound being measured.

$V_o$  = volume of water extracted ( $\text{mL}$ ).

$V_i$  = volume of extract injected ( $\mu\text{L}$ ).

Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: the areas  $A_x$  and  $A_{is}$  should be from the total ion chromatograms and the RF for the compound should be assumed to equal 1. The concentration obtained using this method should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

Report results without correction for recovery data in  $\mu\text{g/L}$  of each PAH.

## 12.0 References

American Society for Testing and Materials. 1984. Annual Book of ASTM Standard Specifications for Reagent Water, D-1933-77. ASTM, Philadelphia, PA.

J.W. Eichelberger, L.E. Harris, and W.L. Budde. 1975. Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry. Anal. Chem. 47:995.

National Oceanic and Atmospheric Administration. 1985. Standard Analytical Procedures of the NOAA National Analytical Facility 1985-1985: Extractable toxic organic compounds. 2nd ed. NOAA Tech. Memo. NMFS F/NWC-92.

U.S. EPA. 1986. Test Methods for Evaluation of Solid Wastes, 3rd edition.  
Office of Solid Waste and Emergency Response, U.S. Environmental  
Protection Agency, Washington, D.C.

Table 1. Characteristic Ions for PAHs.

Compound	Retention Time (min)	Primary Ion Secondary Ion(s)	
Acenaphthene	15.13	154	153, 152
Acenaphthene-d <sub>10</sub> (SS)	15.05	164	162, 160
Acenaphthylene	14.57	152	151, 153
Anthracene	19.77	178	176, 179
Benzo(a)anthracene	27.83	228	229, 226
Benzo(b)fluoranthene	31.45	252	253, 125
Benzo(k)fluoranthene	31.55	252	253, 125
Benzo(g,h,i)perylene	41.43	276	138, 277
Benzo(a)pyrene	32.80	252	253, 125
Chrysene	27.97	228	226, 229
Dibenz(a,h)anthracene	39.82	278	139, 279
Fluoranthene	23.33	202	101, 203
Fluorene	16.70	166	165, 167
Indeno(1,2,3-cd)pyrene	39.52	276	138, 227
2-Methylnaphthalene	11.87	142	141
Naphthalene-d <sub>8</sub> (SS)	9.75	136	68
Perylene-d <sub>12</sub> (SS)	33.05	264	260, 265
Phenanthrene	19.62	178	179, 176
Pyrene	24.02	202	200, 203
Tetrachloro-m-xylene (IS)			

IS = internal standard

SS = surrogate spike

<sup>a</sup>estimated retention times.

Table 2. DFTPP Key Ions and Ion Abundance Criteria<sup>a</sup>

<u>Mass</u>	<u>Ion Abundance Criteria</u>
51	30-60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30 of mass 198
365	>1% of mass 198
441	Present but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

a = from Eichelberger et al., 1975.

## Attachment A - Sephadex LH-20 Column Packing and Recycling

### A.1 Column Packing

1. Fit a 19 mm ID column with a stopcock, add 10 mL of 6:4:3 solvent and between 5 and 10 mm glass wool plug. Tamp the plug to remove any air bubbles.
2. Add approximately 1 mL of sand to the column, and tap the column gently so that the sand forms a smooth layer on top of the glass wool.
3. Pour the swelled Sephadex gel through the funnel into the column until the gel fills the column and about 1/4 of the reservoir.
4. Allow 10 min for the Sephadex to settle. Open the stopcock, and elute 80 mL of solvent to ensure firm packing. Add more solvent as needed. Leave 30 mL of solvent in the column reservoir. Cover the top with aluminum foil, and allow the packing to settle overnight.
5. Open the stopcock, and elute 10 mL of solvent, then close the stopcock. Remove the excess Sephadex packing from the top with a transfer pipet until the height of the Sephadex is 26.5 cm.
6. Gently add approximately 1 mL of sand onto the packing so that it forms an even layer on the top. (The column may be tapped or tilted slightly to get an even layer of sand.)
7. Examine the packing for air bubbles. If bubbles are evident, elute approximately 250 mL of warm (about 35° C) solvent through the column. If the bubbles persist, recycle the packing (see section A.2).

### A.2 Recycling Sephadex LH-20 Column Packing

**NOTE:** When the column no longer maintains its calibration with azulene/perylene, recycle the packing.

1. Decant any solvent in the column reservoir.
2. Empty the column packing into a beaker 4 times the volume of the packing.
3. Wash with  $\text{CH}_2\text{Cl}_2$ .
4. Add enough  $\text{CH}_2\text{Cl}_2$  to float Sephadex particles in the upper half of the beaker.
5. Remove all glass wool with forceps (mandatory).
6. Cover the beaker and let stand for 1 to 2 hours.
7. Decant the floating particles leaving the sand in the beaker.
8. Aspirate the  $\text{CH}_2\text{Cl}_2$  from the Sephadex particles and set them aside.
9. Swell these particles overnight in 6:4:3 solvent before reusing.