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U.S. Army Corps of Engineers

New England District
Concord, Massachusetts

Technical Support Services
General Electric (GE) Housatonic River Project
Pittsfield, Massachusetts

Contract No. DACW33-94-D-0009

Task Order No. 0032

QUALITY ASSURANCE PROJECT PLAN

Volume II
Appendix A

DCN: GEP2-100598-AADE

October 1998

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FINAL

QUALITY ASSURANCE PROJECT PLAN

GENERAL ELECTRIC (GE) HOUSATONIC RIVER PROJECT PITTSFIELD, MASSACHUSETTS

Volume II—Appendix A

Contract No. DACW33-94-D-0009
Task Order No.: 0032
DCN: GEP2-100598-AADE

Prepared for

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TABLE OF CONTENTS

APPENDIX A—STANDARD OPERATING PROCEDURES

Appendix A-1—Standard Operating Procedure for Hardness, Total

Appendix A-2—Standard Operating Procedure for Total Dissolved Solids (Residue, Filtered)

Appendix A-3—Standard Operating Procedure for Total Suspended Solids (Residue, Non-Filtered

Appendix A-4—Standard Operating Procedure for Alkalinity as $CaCO_3$ (Titrimetric, pH 4.5)

Appendix A-5—Standard Operating Procedure for Total and Amenable Cyanide

Appendix A-6—Standard Operating Procedure for Ammonia-Nitrogen

Appendix A-7—Standard Operating Procedure for Total Kjeldahl Nitrogen

Appendix A-8—Standard Operating Procedure for Nitrate/Nitrite-N Method

Appendix A-9—Standard Operating Procedure for Nitrite-N

Appendix A-10—Standard Operating Procedure for Phosphate as P

Appendix A-11—Standard Operating Procedure for Orthophosphate as P

Appendix A-12—Standard Operating Procedure for Sulfide (Method 376.2/4500-S^2-D)

Appendix A-13—Standard Operating Procedure for Sulfide in Soil

Appendix A-14—Standard Operating Procedure for Biological Oxygen Demand

Appendix A-15—Standard Operating Procedure for Total Organic Carbon

Appendix A-16—Standard Operating Procedure for Total Organic Carbon in Sediment (Lloyd Kahn Method)

Appendix A-17—Standard Operating Procedure for Percent Solids

Appendix A-18—Standard Operating Procedure for Acid Digestion of Aqueous Samples for Total Metals

Appendix A-19—Standard Operating Procedure for Acid Digestion of Sediments, Sludges, and Soils for Total Metals

Appendix A-20—Standard Operating Procedure for Metals Analysis by ICP

Appendix A-21—Standard Operating Procedure for Mercury Preparation and Cold Vapor Analysis of Aqueous Samples

Appendix A-22—Standard Operating Procedure for Mercury Preparation and Cold Vapor Analysis of Soil Samples

Appendix A-23—Standard Operating Procedure for Organochlorine Pesticides by Gas Chromatography

TABLE OF CONTENTS
(Continued)

Appendix A-24—Standard Operating Procedure for Polychlorinated Biphenyls (PCB) Analysis

Appendix A-25—Standard Operating Procedure for Organophosphorus Pesticides by Capillary GC

Appendix A-26—Standard Operating Procedure for Chlorinated Herbicides by ECD

Appendix A-27—Standard Operating Procedure for Purge and Trap of Aqueous Samples

Appendix A-28—Standard Operating Procedure for Extractable Semivolatile Organic Compounds by GC/MS

Appendix A-29—Standard Operating Procedure for Extractable PAHs by GC/MS Selective Ion Monitoring

Appendix A-30—Standard Operating Procedure for Petroleum Hydrocarbons (by Infrared Spectrophotometry)

Appendix A-31—Standard Operating Procedure for Ignitability

Appendix A-32—Standard Operating Procedure for Reactivity (Cyanide/Sulfide)

Appendix A-33—Standard Operating Procedure for pH

Appendix A-34—Standard Operating Procedure for Volatile Organic Compounds by GC/MS

Appendix A-35—Standard Operating Procedure for Particle Size Analysis

Appendix A-36—Standard Operating Procedure for Polychlorinated Dibenzo Dioxin/Furans

Appendix A-37—Standard Operating Procedure for Polychlorinated Biphenyls and 1,2,4-TCB by GC-ECD (Modified EPA 8082)

Appendix A-38—Standard Operating Procedure for High Resolution Mass Spectrometry Modified Method 1668

Appendix A-39—Standard Operating Procedure for Chlorophyll-A

Appendix A-40—Standard Operating Procedure for Atterberg Limits (Liquid Limit, Plastic Limit, and Plasticity Index in Soil)

Appendix A-41—Standard Operating Procedure for Specific Gravity (for Use in Porosity Calculation)

APPENDIX A

STANDARD OPERATING PROCEDURES

APPENDIX A-1

STANDARD OPERATING PROCEDURE FOR HARDNESS, TOTAL

Hardness, Total
Method 130.2

Approvals and Signatures

QA Officer: Martha E. Roy Date: 10/3/94

Wet Chemistry Manager: [illegible] Date: 3 Oct 94

1.0 Scope and Application

1.1 This method describes protocols for the determination of Total Hardness in aqueous samples.

1.2 The detection limit may vary with the sample type however, the typical reporting limit is 2.0 mg/l as $CaCO_3$. Homeowners may want their results reported as grains/gallon. The conversion factor for this can be found in the Calculation Section.

2.0 Summary of Method

2.1 Calcium and magnesium ions are segregated from the sample upon the addition of disodium ethylenediamine tetraacetate (Na_2EDTA). The end point of the reaction is detected by use of the indicator: Eriochrome Black T, which has a red color in the presence of calcium and magnesium and a blue color when the cations are removed.

3.0 Sample Handling and Preservation

3.1 A minimum of 100 mls of sample must be collected in preserved plastic or glass containers. The sample is preserved to pH <2 with HNO_3.

4.0 Reagents

4.1 Buffer Solution:

Dissolve 33.8 gram NH_4Cl in 286 ml concentrated NH_4OH in 500 ml volumetric flask. Add 2.5 g MgEDTA (must use magnesium salt here!). Dilute to 500 ml with DIH_2O. Dilute to 500 ml with DIH_2O. Store in plastic bottle. Discard when 1-2 ml added to sample fails to produce a pH of 10.0± 0.1at endpoint of titration.

4.2 Eriochrome Indicator:

0.5 gram Eriochrome Black T plus 100 gram NaCl. Mix thoroughly until a uniform purple color is achieved.

4.3 EDTA Titrant (0.2N):

3.723 gram Disodium EDTA plus DIH_2O to 1 liter standardize against calcium standard obtained from metals lab.

4.4 Ammonium Hydroxide, 1N:

70 ml NH_4OH plus DiH_2O to 1 liter.

5.0 Sample Handling and Preservation

5.1 Collect a minimum of 100 mls of sample in plastic or glass containers. Store at 4 °C; HNO_3 added to pH <2.0.

5.2 Holding time is 28 days from collection.

6.0 Procedure

6.1 Pipette 50 ml sample into white porcelain dish reserved for this analysis. Add stir bar and add 1 N NH_4OH until pH is approximately 7 (use pH paper). Add 1-2 ml Buffer solution and 1-2 scoops of indicator and stir gently. A strong pink color should quickly develop.

6.2 Titrate with EDTA until pink color has turned to purple. Add EDTA very slowly as purple color approaches blue. Add EDTA dropwise at 3-5 second intervals

until the last of the red is gone leaving a blue endpoint. The last drop may actually seem to lighten the color a bit as the final blue is more pale than the purple color you have been watching.

Note 1: Add buffer and indicator so that a clear, obvious pink color develops. Do not add so little that any sample color interferes with the pink to blue titration, or so much that the colors are difficult to distinguish.

Note 2: EDTA volume should not exceed 15 ml. If so, repeat with smaller sample volume.

6.0 Calculations

6.1 CaCO3/l calculations

$$\text{Hardness (EDTA) equiv. mg CaCO3/l} = \frac{A \times N \times 50{,}000}{\text{ml sample}}$$

where: A = ml EDTA titrant
N = normality of EDTA titrant

Note: Standard EDTA titrant is 0.02N.

6.2 Conversion to grains/gallon

Hardness as grains/gallon = Hardness (EDTA)mg CaCO3/l x 0.0584

7.0 Quality Assurance

7.1 A method blank (consisting of DI water) must go through the same procedures as the samples and be less than the reporting limit of 2.0 mg/l.

7.2 An independent check standard (LCS) must be analyzed with each batch of samples and have a recovery of between 90-110%.

7.3 A replicate and matrix spike analysis are performed with each batch of 20 or less samples. The matrix spike recovery should be between 75-125%, and the replicate analysis should have an RPD <20%.

APPENDIX A-2

STANDARD OPERATING PROCEDURE FOR TOTAL DISSOLVED SOLIDS (RESIDUE, FILTERED)

Total Dissolved Solid (Residue, Filterable) Method 160.1 (Gravimetric, Dried at 180°C)

Approvals and Signatures

QA Officer: Martha Roy Date: 7/30/96

Wet Chemistry Section Head: Paul E. Needham Date: 7/30/96

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1. Scope and Application

   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

   1.2 The practical range of the determination is 10mg/l to 20,000 mg/L.

   1.3 The reporting limit is 2.0 mg/L based on 100 mL sample volume.

2. Summary of Method

   2.1 A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180 °C.

   2.2 If residue, non-filterable is being determined, the filtrate from that method may be used for residue, filterable.

3. Definitions

   3.1 Filterable residue is defined as those solids capable of passing through a glass fiber filter and dried to constant weight at 180 °C.

4. Sample Handling and Preservation

   4.1 A minimum of 100 mLs of sample should be collected in plastic or glass

unpreserved containers. Refrigeration or icing to 4 °C to minimize microbiological decomposition of solids, is recommended.

4.2 Samples must be analyzed within 24 hours of collection.

5. Interferences

5.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.

5.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180 °C to insure that all the bicarbonate is converted to carbonate.

5.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.

6. Apparatus

6.1 Glass fiber filter discs, 4.7 cm without organic binder, Reeve Angel type 934-AH, Gelman type A/E, or equivalent.

6.2 Filter holder, membrane filter funnel or Gooch crucible adapter.

6.3 Suction flask, 500 mL.

6.4 250 mL side-arm Erlynmeyer Flasks. A number of these are kept in the 180 °C oven ready for use.

6.5 Drying oven, 105°C ± 3°C.

6.6 Drying oven, 180°C ± 2°C.

6.7 Desiccator.

6.8 Analytical balance, capable of weighing to 0.1 mg.

7. Procedure

7.1 Preparation of glass fiber filter disc: place the disc on the membrane filter apparatus. While vacuum is applied, wash the disc with three successive 20 mL volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard washings. Place washed filters in crucible, dry overnight at 550° C and store desiccated at room temperature.

7.2 Clean 250 mL side-arm flasks are kept in the 180°C oven. Cool the required number of flasks in the desiccator for at least 1 hour. Weigh immediately before use. Wait 15 minutes and then weigh again. Both readings should be the same. The second weighing is used in calculations.

7.3 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 mL to the funnel using a class A volumetric pipet and filter through the glass filter.

7.4 Rinse filter with three (3) 10 mL rinses of DI water. Final volume of sample and washes is approximately 130 mL.

7.5 To prevent splattering, take sample to dryness in 105°C oven overnight, then transfer to 180°C oven.

7.6 Dry in 180°C oven for a minimum of 16 hours. Cool in a desiccator and weigh to the nearest 0.1 mg. Wait 15 minutes and then weigh again. Both readings should be the same. The second weighing is used in calculations.

8. Calculation

8.1 Calculate filterable residue as follows:

$$mg/L = \frac{(A - B) * 1000}{C}$$

where:

A = weight of dried residue + dish in mg
B = weight of dish in mg
C =volume of sample used in mL

9.0 Quality Control

9.1 A replicate analysis is performed with each batch of samples. The RPD for the replicates should be <20%.

9.2 A method blank is prepared and analyzed with each batch of samples. The method blank consists of 100 mL of DI water filtered and carried through the entire process. The method blank must be less than the reporting limit.

9.3 A Laboratory Control Sample (LCS) is prepared and analyzed with each batch of samples. The LCS consists of 0.1000 gram of NaCL dried at 105°C and diluted to 2000 mL. The true value of this LCS is 50 mg/L. The LCS recovery must be between 90-110% or the batch must be reanalyzed.

APPENDIX A-3

STANDARD OPERATING PROCEDURE FOR TOTAL SUSPENDED SOLIDS (RESIDUE, NON-FILTERED)

Total Suspended Solids
Residue, Non-Filterable
Method 160.2 (Gravimetric, Dried at 103-105°C)

Approvals and Signatures

QA Manager: Kim B. Watson Date: 9/4/97

Wet Chemistry Section Manager: David E. Meechan Date: 9-05-97

1.0 Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.2 The practical range of the determination is 4mg/L to 20,000 mg/L. The detection limit is 0.5 mg/L based on a 1000 mL sample volume.

2.0 Summary of Method

2.1 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.

2.2 The filtrate from this method may be used for filterable residue.

3.0 Definitions

3.1 Residue, non-filterable, is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103-105°C.

4.0 Sample Handling and Preservation

4.1 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.

4.2 Collect at least 1 liter of sample in a plastic or glass bottle. The sample should not be preserved. Refrigeration or icing to 4 °C to minimize microbiological decomposition of solids is recommended. The sample must be analyzed within 7 days of collection.

5.0 Interferences

5.1 Filtration apparatus, filter material, pre-washing, post-washing and drying temperature are specified because the variables have been shown to affect the results.

5.2 Samples high in filterable residue (dissolved solids), such as saline waters, brines and some wastes may be subject to a positive interference. Care must be taken in selecting the filtering apparatus so that washing of the filter and any dissolved solids in the filter (7.5) minimizes this potential interference.

6.0 Apparatus

a. Glass fiber filter discs, without organic binder, such as Millipore AP-40, Reeves Angel 934-AH, Gelman 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.

b. Filter support: filtering apparatus with reservoir and a coarse (40-60 microns) 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.

c Suction flask.

d. Drying oven, 103-105°C.

e. Desiccator.

f. Analytical balance, capable of weighing to 0.1 mg.

7.0 Procedure

7.1 Preparation of glass fiber filter disc: place the glass fiber filter on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible with wrinkled surface up. While vacuum is applied, wash the disc with three successive 20 mL volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used, and dry in an oven at 103-105 °C for one hour. Remove to desiccator and store until needed. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg). Weigh immediately before use. After weighing, handle the filter or crucible/filter with forceps or tongs only.

7.2 Selection of sample volume: for a 4.7 cm diameter filter, filter 100 mL of sample. 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. If other filter diameters are used, start with a sample volume equal to 7 mL/cm2 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: Use an unweighed glass fiber filter of choice affixed in the filter assembly. 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. Continue to record the time and volume increments until filtration rate drops rapidly. Add additional sample if the filter funnel volume is inadequate to reach a reduced rate. Plot the observed time versus volume filtered. Select the proper filtration volume as that just short of the time a significant change in filtration rate occurred.

7.3 Assemble the filtering apparatus and begin suction. Wet the filter with a small volume of distilled water to seat it against the fritted support.

7.4 Shake the sample vigorously and quantitatively transfer the predetermined sample volume selected in 7.2 to the filter using a graduated cylinder. Remove all traces of water by continuing to apply vacuum after sample has passed through.

7.5 With suction on, wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with three portions of distilled water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum after water has passed through.

NOTE: Total volume of wash water used should equal approximately 2 mL per cm2. For a 4.7 cm filter the total volume is 30 mL.

7.6 Carefully remove the filter from the filter support. Alternatively, remove crucible and filter from crucible adapter. Dry the filter for at least 16 hours at 103-105 °C. Drying for 16 hours rather than one hour increments ensures completeness of the drying cycle so repetitive drying may not be required. Cool in a desiccator and weigh to the nearest 0.1 mg. Wait 15 minutes and then weigh again. Both readings should be less than 4% of the previous weight or 0.5 mg whichever is less. If this criteria is not met then the sample must be reheated and reweighed until the both readings are less than 4% of the previous weight. The second weighing is used in calculations. Record all weighs, and time in and out on the Solids Benchsheet.

8.0 Calculations

8.1 Calculate non-filtered residue as follows:

$$\text{Non-filterable residue, mg/l} = \frac{(A-B) \times 1000}{C}$$

where:
A = weight of filter (or filter and crucible) + residue in mg
B = weight of filter (or filter and crucible in mg
C = mL of sample filtered

9.0 Quality Control

9.1 A replicate analysis is performed with each batch of samples. The RPD for the replicates should be <20%.

References:

Standard Methods for the Examination of Water and Wastewater, 18th Edition. Edited by Greenberg, Clesceri, and Eaton. 1992.

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APPENDIX A-4

STANDARD OPERATING PROCEDURE FOR ALKALINITY AS $CaCO_3$ (TITRIMETRIC, pH 4.5)

Alkalinity as $CaCO_3$ (Titrimetric, pH 4.5)
Method 310.1

Approvals and Signatures

QA Officer: Martha Ray Date: 7/30/96

Wet Chemistry Section Head: Daniel E. Meadow Date: 7/30/96

1.0 Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.2 The method is suitable for all concentration ranges of alkalinity; however, a titration volume of 50 mLs is generally used. An aliquot of 100 mLs is used for low level samples.

1.3 The reporting limit for this method is 1.0 mg/L as $CaCO_3$.

2.0 Summary of Method

2.1 An unaltered sample is titrated to an endpoint of pH 4.5; determined by a pH meter. The sample must not be filtered, diluted, concentrated, or altered in any way.

3.0 Interferences

3.1 Substances, such as salts of weak organic and inorganic acids present in large amounts, may cause interference in the electrometric pH measurements.

3.2 Oil and grease, by coating the pH electrode, may also interfere, causing sluggish response.

4.0 Sample Handling and Preservation

4.1 A minimum sample volume of 100 mLs is needed. The sample is collected in a non-preserved bottle.

4.2 The sample should be refrigerated at 4°C and run as soon as practical. The sample bottle should not be opened prior to analysis.

4.3 Holding time is 14 days from collection.

5.0 Apparatus and Reagents

5.1 pH meter that uses a glass electrode and can be read to 0.05 pH units. The meter should than be standardized and calibrated according to manufacturer's instructions. If automatic temperature compensation is not provided, make titration at 25±2°C.

5.2 Magnetic stirrer, pipets, flasks and other standard laboratory equipment.

5.3 Burets, Pyrex 50 mL.

5.4 0.02 N H_2SO_4 purchased as a prepared reagent. Certification is supplied with each lot.

6.0 Procedure

6.1 Sample size

6.1.1 Use a sufficiently large volume of titrant (>20 mL in a 50 mL buret) to obtain good precision while keeping volume low enough to permit sharp end point.

6.1.2 For <1000 mg $CaCO_3$/L use 0.02 N titrant

6.2 Potentiometric titration

6.2.1 Place sample in flask by pipetting with pipet tip near bottom of flask.

6.2.2 Measure the pH of sample.

6.2.3 Add standard acid, being careful to stir thoroughly but gently to allow needle to obtain equilibrium.

6.2.4 Titrate to pH 4.5. Record volume of titrant.

6.3 Potentiometric titration of low alkalinity

6.3.1 For alkalinity of <20 mg/L titrate 100-200 mL as above (7.2) using a 10 mL microburet and 0.02 N acid solution.

6.3.2 Stop titration at pH in range of 4.3-4.7, record volume and exact pH. Very carefully add titrant to lower pH exactly 0.3 pH units and record volume.

7.0 Calculations

7.1 Potentiometric titration to pH 4.5

$$Alkalinity\ (mg/L\ CaCO3) = \frac{A * N * 50{,}000}{mL\ of\ sample}$$

where: A = mL standard acid
N = normality standard acid

7.2 Potentiometric titration of low alkalinity:

$$Alkalinity\ (mg/L\ CaCO3) = \frac{(2B-C) * N * 50{,}000}{mL\ of\ sample}$$

where: B = mL titrant to first recorded pH
C = total mL titrant to reach pH 0.3 units lower
N = normality of acid

8.0 Quality Control

8.1 A Laboratory Control Sample (LCS) must be analyzed with every batch. The recovery of the LCS must be within 80-120%. If the control limit is exceeded the batch must be reprepared.

8.2 A method blank must be analyzed with every batch. The results of the method blank must be less than the reporting limit. If the method blank results are above the reporting limit the batch must be repeated unless the sample results are >10 times the blank concentration.

8.3 A replicate and matrix spike are prepared and analyzed with every batch. The RPD recovery must be $\leq 20\%$. The matrix spike recovery must be within 75-125%. If either control limit is not met the analysis is repeated.

APPENDIX A-5

STANDARD OPERATING PROCEDURE FOR TOTAL AND AMENABLE CYANIDE

Total and Amenable Cyanide
Methods 335.1, 335.2 and 9010

Approvals and Signatures

QA Manager: Martha Roy Date: 6/23/97

Inorganics Section Head: Kristine L. Aubin Date: 6/23/97

1.0 Scope and Application

1.1 This method describes protocols for the determination of Total Cyanide in aqueous samples and sediments.

1.2 Detection Limit: 10 ug/l (0.01 mg/L) for liquid samples
0.5 mg/Kg on an "as received" basis for solids.

2.0 Summary of Method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.

2.2 The cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed by the addition of pyridine-barbituric acid reagent.

2.3 Treatment for cyanide amenable to chlorination is described in Appendix A, Section 10.0.

3.0 Interferences

3.1 Interferences are eliminated or reduced by using the distillation procedure. Chlorine and sulfide are interferences.

3.2 Oxidizing agents such as chlorine decompose most cyanides. Chlorine interferences can be removed by adding an excess of ascorbic acid to the waste prior to preservation and storage of the sample.

3.3 Sulfide interference can be removed by adding an excess of bismuth nitrate to the waste (to precipitate the sulfide) before distillation. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation should be treated by the addition of bismuth nitrate.

3.4 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds once formed will decompose under test conditions to generate HCN. The possibility of interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation. Nitrate and nitrite are interferences when present at levels higher than 10 mg/L and in conjunction with certain organic compounds.

3.5 Thiocyanate is reported to be an interference when present at very high levels. Levels of 10 mg/L were not found to interfere.

3.6 Fatty acids, detergents, surfactants, and other compounds may cause foaming during the distillation when they are present in large concentrations and will make the endpoint of the titration difficult to detect. They may be extracted at pH 6-7.

4.0 Sample Handling and Preservation

4.1 Minimum sample volume is 500 mL for liquid samples, or 5 grams for solid and soil samples. Holding time for any matrix is 12 days from sample receipt.

4.2 Sample Preservation: 10 pellets of NaOH and 0.6 grams ascorbic acid per liter. The pH of aqueous samples must be determined prior to analysis. Should pH be less than 12, additional NaOH is added. The project director must be notified should this occur. Soil samples are not preserved.

4.3 Collect samples in plastic bottles. Cool and maintain at 4±2 °C.

5.0 Reagents and Equipment

All prepared standards and reagents are assigned an expiration date of six (6) months from the date of preparation; unless the expiration date of the parent solution expires sooner than that expiration date is used. All standards and reagents are stored at room temperature unless otherwise noted. The preparation of all standards is recorded in the wet chemistry standard preparation notebook.

5.1 1000 mg/L CN Standard Stock: 2.51 gram KCN and 2.00 gram KOH plus DIH_2O to one liter. Concentration checked weekly by titration with $AgNO_3$. Store in refrigerator at 4 ± 2°C.

5.2 10 mg/L CN Intermediate Standard: 10 mL 100 mg/L CN stock and 10.00 gram NaOH plus DIH_2O to one liter. Prepare daily.

5.3 1.0 mg/L CN Working Standard: 10 mL 10 mg/L intermediate standard and 1.00 gram NaOH plus DIH_2O to 100 mL. Prepare daily.

5.4 500 mg/L CN Check Standard Stock: 0.6278 gram KCN and 1.00 gram KOH plus DIH_2O to 500 mL. Use only the KCN reserved for check standard purposes - this is a different source than that used for the 1000 mg/L stock above. The concentration of this stock is also checked weekly by titration with $AgNO_3$. Store in refrigerator at 4 ± 2°C.

5.5 10 mg/L CN Check Standard, Intermediate Standard: 5 mL 500 mg/L stock and 2.50 grams NaOH plus DIH_2O to 250 mL.

5.6 1.0 mg/L CN Check Standard, Working Standard: 10 mL 10 mg/L check standard intermediate and 1.00 gram NaOH plus DIH_2O to 100 mL.

5.7 25 mg/L CN Soil Spiking Standard: 5 mL 1000 mg/L CN standard stock and 2.00 gram NaOH plus DIH_2O to 200 mL.

5.8 2.5 N NaOH: 800.0 grams NaOH plus DIH_2O to 8 liters. Store in plastic carboy.

Note: All methods call for 50 mL of 1.25 N NaOH per impinger. The laboratory impingers are not able to hold 50 mL. The method has been modified to accommodate this by using 25 mL of 2.5 N NaOH. Extensive experience with this system has shown acceptable cyanide recoveries using this

modification.

5.9 0.25 N NaOH: 100 mL 2.5 N NaOH plus DIH_2O to one liter.

5.10 Sulfamic Acid Solution: 380.0 grams sulfamic acid plus DIH_2O to one gallon. Store in plastic carboy.

5.11 50% H_2SO_4: 1000 mL concentrated H_2SO_4 slowly added to 1000 mL DIH_2O with constant stirring. Allow to cool before using.

5.12 Magnesium Chloride Solution: 2.5 Kg $MgCl_2$-$6H_2O$ plus DIH_2O to 4900 mL in plastic carboy.

5.13 Phosphate Buffer: 138 grams NaH_2PO_4-H_2O plus DIH_2O to one liter. De-aerate for one hour prior to use.

5.14 Pyridine-Barbituric Acid Reagent: 150 grams barbituric acid and 750 mL pyridine in approximately one liter of DIH_2O. Slowly add 150 mL concentrated HCl, with stirring. Bring to 2500 mL with DIH_2O. Store in amber glass in refrigerator. Prepare a working solution by combining 200 mL stock with 600 mL DIH_2O. Mix and de-aerate for one hour prior to use.

5.15 Chloramine-T reagent: 4.0 g chloramine-T plus DIH_2O to one liter. De-aerate for one hour prior to use.

5.16 Soil Laboratory Control Sample (LCS): Our soil LCS is obtained through Environmental Resource Associates. Only one lot is in use at a time and expiration dates are strictly adhered to. The LCS is stored in the refrigerator. LCS results are reported on an "as received" basis.

5.17 Equipment: Leeman Labs PS1214, Automated cyanide analyzer. System includes an autosampler and a personal computer.

6.0 Distillation Procedure

6.1 All glassware must be thoroughly rinsed with DIH_2O prior to use.

6.2 Add 25 mL 2.5 N NaOH to each impinger and place impingers in their holders.

6.3 Each analysis must consist of a distilled blank (500 mL DIH_2O), a 120 ug/l ICV (6 mL of the 10 mg/L Cyanide Stock Standard, see Section 4.5, plus DIH_2O to 500 mL), a 40 ug/l LICV (2 mL of the 10 mg/L Cyanide Stock Standard, see Section 4.5, to DIH_2O to 500 mL) and up to 20 liquid samples. When soil samples are to be analyzed, a soil prep blank and a soil LCS must be included. Approximately 1-2 grams of beach sand and a commercially prepared soil LCS are used for each.

Note: Both methods 335.2 and 9010A recommend the distillation of two known standards (at high and low concentrations). The laboratory feels this allows us to better document the efficiency of the distillation procedure. These standards are designated ICV and LICV (for "low ICV").

Make sure to check that the pH of all liquid samples is ≥ 12- Record the pH on the benchsheet.

6.4 Check all liquid samples for chlorine with potassium iodide starch test paper. The test paper will turn dark if chlorine is present in the sample. Notify the wet chemistry group leader if this happens.

Place sample flasks in the appropriate heating mantles and connect all tubing. Make sure all glass connections are tight.

6.5 Turn on the vacuum and adjust each station for maximum flow, but without drawing NaOH up into the impinger head. Allow system to equilibrate for 5 minutes and recheck flow rates.

6.6 Slowly pour 20 mL sulfamic acid solution down the thistle tube for each station. Wait 3 minutes. Pour 50 mL 50% H2SO4 into each sample. Pour slowly and watch for any reaction that may occur upon contact with the sample. Allow to mix for 5 minutes. Now add 20 mL magnesium chloride. Follow with a short rinse of DIH2O.

Note: Both methods 335.2 and 9010A recommend the addition of sulfamic acid to eliminate positive interference in samples known or suspected to contain nitrite or nitrate. As this addition causes no interference of its own, and we must suspect that most of our samples contain at least some nitrate, we have adopted the policy of adding sulfamic acid to all blanks, distilled standards and samples.

6.7 Turn on the heating units and reflux for 2 hours. Begin timing only after samples are at a near-boil. Check the vacuum in each impinger frequently, making adjustments as needed. Following reflux, allow the samples to cool for 30 minutes while still under vacuum.

6.8 Quantitatively transfer the impinger contents to a 250 mL volumetric flask. Take care to thoroughly rinse all inside surfaces of the impinger, especially the interior of the fritted tube. Bring to volume with DIH_2O and mix by inversion.

7.0 Distillate Analysis Procedure

7.1 Test each sample distillate for the presence of sulfide using lead acetate paper. Sulfide produces a milky appearance with the addition of chloramine-T, resulting in a positive interference, and must be removed prior to analysis.

Note: When a distillate contains sulfide, producing a brown/black color on the lead acetate paper, add a scoop of cadmium carbonate to an aliquot of the distillate and mix by inversion. Sulfide is removed as the yellow precipitate cadmium sulfide. Re-test with lead acetate paper, adding more cadmium carbonate until the paper stays clear. The distillate must be filtered before analysis.

7.2 Prepare the cyanide standard curve, using 1 mg/L (Section 5.3) and 10 mg/L standards (Section 5.2) , as follows:

mLs of 1 mg/L Cyanide standard used	mLs of 0.25 N NaOH used	Final curve concentration (ug/L)
---	----	0 (Blank) DI Water
1.0	99.0	10
5.0	95.0	50

mLs of 10 mg/L Cyanide standard used	mLs of 0.25 N NaOH used	Final curve concentration (ug/L)
1.0	99.0	100
2.0	98.0	200
3.0	97.0	300
4.0	96.0	400

The curve is to be prepared fresh daily. The 1000 mg/L stock (Section 5.1) from which all standards are prepared is to be verified weekly by $AgNO_3$ titration.

7.3 Prepare a continuing calibration verification (CCV) by pipetting 15 mL 1 mg/L check standard (Section 4.6) into a 100 mL volumetric flask and bring to volume with 0.25 N NaOH. For initial calibration verification (ICV) prep see Section 6.3.

7.4 Blanks: Preparation Blanks (Method Blanks) see Section 5.3.
ICB/CCB (Calibration Blanks)= DIH_2O not distilled.

7.5 Distillates are analyzed using the Leeman PS 1214 cyanide analyzer. Refer to the operators manual for complete details on the instruments use. See Appendix A for the order of analysis when using the Leeman PS1214.

8.0 Calculation

Liquids

$$C_{(mg/L)} = \frac{ug}{L_{dist}} * \frac{V_{dist}}{V_{samp}} * \frac{1\,mg}{1000\,ug}$$

Where:
ug/L_{dist} = Leeman PS1214 result including all dilution factors
V_{dist} = final distillate volume in liters
V_{samp} = sample volume in liters

Example

$$0.025_{(mg/L)} = \frac{50\,ug}{L_{dist}} * \frac{0.25\,L}{0.5\,L} * \frac{1\,mg}{1000\,ug}$$

Solids

$$C_{(mg/Kg\ drywt.)} = \frac{ug}{L_{dist}} * \frac{V_{dist}}{g_{samp}} * \frac{100}{\%\ solids}$$

Where:
ug/L_{dist} = Leeman PS1214 result including all dilution factors
V_{dist} = final distillate volume in liters
g_{samp} = sample weight in grams
% Solids = Percent solids to nearest 0.1%

Example

$$1.9_{mg/Kg\ drywt.} = \frac{30\ ug}{L_{dist}} * \frac{0.25\ L}{5.00\ g} * \frac{100}{78.8}$$

9.0 Quality Control

9.1 The standard curve is made up fresh daily. The standard curve consists of a blank, then 10, 50, 100, 200, 300 and 400 ug/l standards. Be sure to record the lot number of the cyanide stock standard solution on the benchsheet. The correlation coefficient of the curve must be ≥0.995.

9.2 Calibration verification standards (CCV's) and calibration blanks (ICB and CCB's) are analyzed every ten samples. CCV's have a control limit of 85-115% of true value. ICB's and CCB's may not exceed ± 10 ug/l.

9.3 One Prep Blank is prepared with each batch of samples of the same matrix. Prep blanks, whether for liquids or solids, must be within the ± 10 ug/l range.

9.4 Soil Laboratory Control Samples (LCS) are prepared with each batch of soil samples. Soil LCS results must fall within the specified range for that lot.

9.5 The ICV is distilled with each batch (regardless of matrix)and must be with the control limits of 85-115%.

9.6 Any sample which exceeds 300 ug/l must be diluted with 0.25 N NaOH and reanalyzed.

9.7 A sample duplicate and a matrix spike are performed with every sample batch of up to 20 samples of the same matrix. Duplicate samples must have an RPD ± 20%. Spike recoveries must be 75-125%. Samples failing the matrix spike criteria must have a post-distillation spike performed on it. Matrix spike recovery is

calculated with the following equation:

$$MS\ Recovery\ (\%) = \frac{SSR - SR}{SA} * 100$$

where:
SSR = Spike Sample Results
SR = Sample Results
SA = Spike Added (concentration)

The Relative Percent Difference (%RPD) between the sample and duplicate analysis is calculated with the following equation:

$$\%\ RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} * 100$$

where:
RPD = Relative Percent Difference
D_1 = First Sample Value
D_2 = Second Sample Value (duplicate)

9.8 Spiking protocols:

For liquid and soil sample: 1 mL 25 mg/L standard distilled with 500 mL/1 gram sample corresponds to 0.1 mg/L (100 ug/l) spike added in distillate. With each spike a post distillate spike is run at 2x detection limit which corresponds to 20 ug/L at instrument. This is used if the spike fails.

9.9 Instrument Detection Limit (IDL) Studies are determined quarterly. The IDL is determined by analyzing a known concentration (not distilled) of standard 7 times on three non-consecutive days and multiplying the standard deviation by 3. The resulting IDL must be less than the reporting limit of 10 ug/l.

In addition Method Detection Limit Studies (MDL) are determined annually. The MDL is determined by taking 7 samples of known concentration of cyanide and analyzing them. These standards are distilled. The standard deviation is then multiplied by 3.143 to determine the MDL. The resulting MDL must be less then the reporting limit of 10 ug/l.

Appendix A:
Amenable to Chlorination Procedure

10.0 Cyanide Amenable to Chlorination

10.1 Procedure

A portion of the sample is chlorinated at a pH > 11 to decompose the cyanide. Cyanide levels in the chlorinated sample are then determined by the method for Total Cyanide explained earlier. Cyanides amenable to chlorination are then calculated by difference.

10.2 Reagents

a. Bleach: (Sodium Hypochlorite): Purchased commercially.

b. Saturated Base: Dissolve 1000 gram NaOH in 1000 gram DIH_2O. Stored in several plastic bottles throughout the wet lab.

c. Potassium Iodide- Starch Paper: Purchased commercially.

d. Ascorbic Acid crystals.

10.3 Procedure

10.3.1 The sample must be divided into two equal aliquots (Preferable 500 mL each); one fraction for total cyanide, the second for chlorination.

10.3.2 500 mL sample in 1 liter beaker on stir plate, under hood, test that the pH is between 11-12. For soil samples use 5.0 grams + DIH_2O to 500 mL.

10.3.3 Add bleach (Na Hypochlorite) "dropwise" until sample tests positive for chlorine (Distinct blue color on KI-starch Paper).

10.3.4 Stir for 1 hour, testing repeatedly for excess chlorine (KI starch paper). Add more bleach to keep distinct blue color- Do not let chlorine disappear! Should KI-Starch give negative result, you must start the hour over again! However, don't just dump in a whole bunch of bleach because you have to neutralize it when you're done.

10.3.5 When the hour is up, add scoops of ascorbic acid until KI-starch paper tests negative... then add one more scoop.

10.3.6 Quantitatively transfer this to a 1000 mL round bottom flak and analyze for cyanide per usual. Designate all amenable cyanide as "_____AM", so as not to be confused with the total cyanide.

10.3.7 Amenable cyanide is actually

Total Cyanide - "AM CN" = Amenable Cyanide

Appendix B:
Leeman PS1214 Automated Cyanide Analyzer, Order of Analysis for All Cyanide Methods:

1. Standard Curve: Blank, 10ppb, 50ppb, 100ppb, 200ppb, 300, 400 ppb Standards (Not Distilled).

2. ICV (Distilled): TV = 120ppb; 240ppb on curve
   Preparation: 6ml 10mg/l Check Standard plus DIH_2O to 500ml.

3. ICB (Not Distilled):DIH_2O

4. CCV (Not Distilled):
   Preparation: 15ml 1mg/l Check Standard plus 0.25N NaOH to 100ml.

5. CCB (Not Distilled):DIH_2O

6. LICV (Distilled): TV = 40ppb; 80ppb on curve
   Preparation: 2ml 10mg/l Check Standard plus DIH_2O to 500ml.

7. PBW: 500 mL DIH_2O

8. PBS: 1-2g Beach Sand (Only if soil samples are included in the batch)

9. LCSS: 1-2g soil LCS (Required mass will depend on the True Value for each Standard Lot. Use only if soil samples are included in the batch.)

10. 7 or 9 Sample Distillates (Depending on whether PBS and LCSS are included)

11. CCV

12. CCB

13. 10 Sample Distillates

14. CCV

15. CCB

16. Last 2 Sample Distillates

17. CCV

18. CCB

APPENDIX A-6

STANDARD OPERATING PROCEDURE FOR AMMONIA-NITROGEN

Ammonia-Nitrogen
Method 350.2

Approvals and Signatures

QA Manager: Kim B. Watson Date: 7/3/97

Wet Chemistry Manager: Daniel E. Moellner Date: 07/03/97

Inorganics Laboratory Manager: Kristene L. Aubin Date: 7/3/97

1.0 Scope and Application

1.1 This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen, in drinking, surface and saline waters, domestic and industrial wastes. A DIH_2O extraction makes this method applicable to soils as well. It is the method of choice where economics and sample load do not warrant the use of automated equipment.

1.2 The method covers the range from about 0.05 to 1.0 mg NH3-N/L for the colorimetric procedure, from 1.0 to 25 mg/L for the titrimetric procedure, and from 0.05 to 1400 mg/L for the electrode method.

1.3 The reporting limit for this method is: Liquids: 0.02 mg/L and
Solids: 2 mg/kg on an "as received" basis.

2.0 Summary of Method

2.1 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 can be determined colorimetrically by nesslerization, titrimetrically with standard sulfuric acid with the use of a mixed indicator, or potentiometrically by the ammonia electrode. The choice between the first two procedures depends on the concentration of the ammonia.

3.0 Sample Handling and Preservation

3.1 A minimum of 500 mL of sample must be collected in preserved plastic or glass containers. Liquid samples are preserved with conc. H_2SO_4 per liter to pH <2 and stored at 4 °C. A minimum of 50 grams of soil should be collected and stored at 4°C.

3.2 The holding time for this method is 28 days from collection.

4.0 Standards and Reagents:

All reagents and solvents used during analysis are of appropriate purity and prior to use will be checked for contamination and documented in the standard preparation logbook. A unique identifier will be assigned to each original stock material and to each subsequent dilution. The preparation logbook will include the prepared concentration and unique identifier of the prepared material, the dates of preparation and expiration, the amount and the lot numbers or unique identifiers of the materials and solvents used to prepare the material, and the identity of the person who prepared the materials. Assigned expiration dates for purchased materials must not exceed the manufacturer's expiration date. Expiration dates for laboratory prepared standards and QC materilas must no exceed the shelf life allowed by the referenced analytical method, if provided.

4.1 <u>1000 mg/L Ammonia Stock</u>:

3.819 g NH_4Cl plus DI water to one liter. Acidify with 3 mL 70% H_2SO_4 .

4.2 <u>2 mg/L Working Standard:</u>

2 mL 1000 mg/L stock plus DI water to one liter. Make fresh for each curve.

4.3 <u>20 mg/L Standard</u>: For calibration verification (ICV, CCV)

76.4 mg NH_4Cl to one liter. Acidify with 3 mL 70% H_2SO_4.
Remember to use the NH_4Cl reserved for Check Standards Only.

4.4 Borate Buffer: Prevents hydrolysis of cyanates and organic nitrogen compounds.

28.5 g Sodium Borate plus DI water to three liters. Bring to pH 9.5-9.8 using saturated NaOH.

4.5 Boric Acid Solution:

76 g Boric Acid plus DI water to one gallon in plastic jug.

4.6 Nessler Reagent:

Purchased commercially. Should have a pale yellow color. Do not use if reagent is cloudy, has an orange color, or has a noticeable orange precipitate.

5.0 Distillation - Using the Labconco Rapid-Still II:

5.1 Turn the distiller on. Check that the boiling flask (visible through the open slot) is at least three-quarters full. If not, add water by setting the swing arm to the "fill" position and turning the valve on the wall. Add the water slowly! This is most important when the boiling flask contains boiling water. After filling, turn off the water valve and return the swing arm to the standby position.

NOTE: When adding water to the boiling flask, there should be no sample distillation vessel in place. A vacuum can develop that will draw sample up into the steam tubing.

5.2 The Borate Buffer is added manually and the pumping apparatus is stored rinsed and empty. Attach the tubing to the gallon jug containing the buffer. With an empty distillation vessel in place, prime the system to fill all tubing with buffer. Discard any buffer now in the distillation vessel.

5.3 Prior to distilling standards or samples, distill a DI water "blank", collecting approximately 200 mL of distillate. Repeat this once or twice. This not only cleans out the distiller, but also "warms up" the system.

5.4 As the water in the boiling flask is heating, prepare the sample and catch flask:

5.4.1 Check that all liquid samples are pH <2 and record on the bench sheet.

5.4.2 Carefully pour 500 mL liquid sample or 5 grams soil and 500 mL DIH_2O, or a standard into a 750 mL distillation vessel.

5.4.3 Add 2-3 drops phenolphthalein indicator.

5.4.4 Add saturated NaOH dropwise (with mixing) to a permanent pink color.

5.4.5 Place the distillation vessel in the holder, close the safety door and immediately add 50 mL Borate Buffer.

5.4.6 Pipette 30 mL Boric Acid Solution into a 500 mL Erlenmeyer catch flask and position so the tip of the condensation tube is submerged.

5.5 When the boiling flask has reached a strong boil, move the swing arm to the distill position. There will be lots of bumping until the sample begins to boil; this is normal. After several minutes, distillate will begin to trickle down the condensation tube and into the catch flask. Allow to distill until the volume in the flask is approximately 275 mL. Return the swing arm to standby.

5.6 Remove the distillation vessel, and discard the spent sample. Be very careful. Allow the last of the distillate to drain into the catch flask and remove.

5.7 The boiling flask should be a little less than half full. In the fill position, add more water, bringing up to three quarters full. Return to standby.

5.8 Transfer the contents of the catch flask to a 500 mL graduated cylinder and bring to 300 mL with DI water. Pour back into the catch flask and mix.

5.9 Nesslerization Procedure:

Prepare an external standard curve using the 2 mg/L working standard (3.b):

Blank	50 mL DI Water
0.04 mg/L	1 mL of 2 mg/L standard + DI Water to 50 mL
0.12 mg/L	3 mL of 2 mg/L standard + DI Water to 50 mL
0.2 mg/L	5 mL of 2 mg/L standard + DI Water to 50 mL
0.4 mg/L	10 mL of 2 mg/L standard + DI Water to 50 mL
0.8 mg/L	20 mL of 2 mg/L standard + DI Water to 50 mL
1.2 mg/L	30 mL of 2 mg/L standard + DI Water to 50 mL
1.6 mg/L	40 mL of 2 mg/L standard + DI Water to 50 mL
2.0 mg/L	50 mL of 2 mg/L standard

5.10 ICV/CCV and ICB/CCB:

Calibration verification standards (ICV/CCV): 1 mL 20 mg/L NH_3-N standard (3.c) plus DI water to 50 mL. True value equals 0.4 mg/L.

Calibration Blanks (ICB/CCB): 50 mL DI water.

5.11 Add 2 mLs Nessler Reagent to each standard or distillate. Mix thoroughly and allow color to develop for 15 minutes.

5.12 Read % T at 425 nm using a 2 cm cuvette. Plot mg/L concentration against log %T.

5.13 Distillates exceeding the upper limit of the standard curve must be diluted and re-analyzed (on the spectrophotometer only- do not redistill). Dilutions should be prepared so as to fall in the top half of the curve.

6.0 Calculations:

6.1 for Liquid samples mg/L = $NH_3\text{-}N/L_{distillate} \times \frac{\text{distillate volume (mL)}}{\text{sample volume (mL)}}$

6.2 for Solid samples mg/kg as rec = $NH_3\text{-}N/L_{distillate} \times \frac{\text{distillate volume (mL)}}{\text{sample volume (g)}}$

Remember solid samples are to be corrected for % solids and reported on a dry weight basis.

7.0 Quality Control

7.1 The standard curve must contain at least 6 points and have a regression of -0.995 or better.

7.2 Immediately following the standard curve, and ICV and ICB must be analyzed. The ICV must fall within 90-110 % recovery and is read directly from the curve. The ICB must be less than 0.04 mg/L.

CCV's and CCB's have the same control limits as stated for the ICV and ICB.

7.3 Every batch of digested samples must contain a blank (PBW) and two Laboratory Control Samples (LCS's). The same LCS will be used, but one will be diluted to fall in the lower half of the standard curve, while the other will be prepared to fall in the upper half. The PBW must be less than the detection limit. The LCS must fall within 85-115 % recovery. The LCS is purchased from a vendor and the true value will very with different lots.

7.4 A duplicate and a matrix spike should be analyzed with each digestion batch. The control limits for the matrix spike analysis is 75-125%. The replicate analysis should have an RPD <20%.

References

1. USEPA EPA-600/4-79-020 Revisied March 1983, Methods For Chemical Analysis of Waters and Wastes, Method 350.2 Issued 1971 Editorial revision 1974

wc3502.wpd

APPENDIX A-7

STANDARD OPERATING PROCEDURE FOR TOTAL KJELDAHL NITROGEN

Total Kjeldahl Nitrogen
Method 351.3

Approvals and Signatures

QA Officer: Martha E. Roy Date: 3/6/95

Wet Chemistry Manager: [illegible] Date: 6 March 95

1.0 Scope and Application

1.1 This method covers the determination of total Kjeldahl nitrogen in drinking, surface and saline waters, domestic and industrial wastes. A DIH_2O extration makes this method applicable to soil samples as well. The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines.

1.2 Ammonia is determined after distillation by the Nesslerization method which is applicable to concentrations below 1 mg N/liter.

1.3 The reporting limit for this method is: 0.2 mg/l for liquid samples and 12 mg/Kg "as received" for solid samples

2.0 Definitions

2.1 Total Kjeldahl nitrogen is defined as the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)2SO_4$, under the conditions of digestion described below.

2.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free- ammonia value (Method 350.2, Nitrogen, Ammonia, this manual) from the total Kjeldahl nitrogen value. This may be determined directly by removal of

ammonia before digestion.

3.0 Summary of Method

3.1 The sample is heated in the presence of conc. sulfuric acid, K_2SO_4 and $HgSO_4$ and evaporated until SO_3 fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled, diluted, and is treated and made alkaline with a hydroxide-thiosulfate solution. The ammonia is distilled and determined after distillation by Nesslerization, titration or potentiometry.

4.0 Sample Handling and Preservation

4.1 A minimum of 100 mls of sample must be collected in preserved plastic or glass containers. Samples are preserved by addition of conc. H_2SO_4 to pH <2 and stored at 4 °C.

4.2 The holding time for this method is 28 days from collection.

5.0 Reagents

5.1 Mercuric Sulfate Solution:

160 grams red Mercuric Oxide dissolved in DI water containing 200 ml concentrated H_2SO_4. Bring to 2 liters with DI water.

5.2 TKN Digestion Reagent:

267 grams K_2SO_4 dissolved in 1300 ml DI water and 400 ml concentrated H_2SO_4. Add 50 ml Mercuric Sulfate solution and bring to 2 liters with DI water.

5.3 Neutralization Reagent:

200 grams $NA_2S_2O_3 \cdot 5\ H_2O$ dissolved in approximately 4 liters DI water. Use the 10 liter carboy reserved for this reagent. With constant stirring, slowly add 2000 grams NaOH pellets.

Caution: This generates a lot of heat! Once all pellets are dissolved, bring to 8

liters with DI water.

5.4 Boric Acid Solution:

Dissolve 160 grams Boric Acid (do not confuse with Sodium Borate) in approximately 6 liters DI water. Use the 10 liter carboy reserved for this reagent. Bring to 8 liters with DI water.

5.5 Ammonium Chloride Standard: 1000 mg NH_3-N/l.

Dissolve 3.819 grams NH_4Cl (pre-dried at 105°C) plus DI water to 1 liter. Acidify with 3 ml 70% H_2SO_4.

5.6 2 mg/l NH_3-N working standard:

2 ml 1000mg/l stock plus DI water to 1 liter. Prepare for each curve.

5.7 20 mg/l Ammonium Chloride for calibration verification:

76.4 mg NH_4CL (pre-dried at 105° C) plus DI water to 1 liter. Use the separate source designated for check standards only. Preserve with 3 ml 70% H_2SO_4.

5.8 Nessler Reagent:

Purchased commercially. Should have a pale yellow color. Do not use if reagent is cloudy, has an orange color, or has a noticeable orange precipitate.

6.0 Digestion Procedure:

6.1 Each digestion batch consists of a Method Blank (Processed Blank), Independent Laboratory Control Sample (LCS) and up to 18 samples. Method Blanks consist of 100 ml of DI water. The LCS is purchased from a vendor and the true value will vary with different lots.

Check that all liquid samples are pH <2. Record on benchsheet.

Use 100 ml for liquid sample (or appropriate dilution where known) and 1 gram for solid samples (add 100 ml DI water to solid samples).

6.2 Slowly add 20 ml Digestion Reagent to each liquid sample and place in block digestor (pre-heated to 380 - 400 °C). Add 50 ml Digestion Reagent to solid samples. A few carborundum #12 granules are added to each flask to prevent excessive bumping.

6.3 To prevent the possibility of "under digesting" samples are digested for up to 4 hours. Before removing from the digestor, visually inspect each flask for a clear or pale yellow color and the presence of white SO_3 fumes, and allow to digest for an additional 30 minutes.

6.4 Allow flasks to cool. Proceed immediately with distillation.

7.0 Distillation Procedure:

Distillation - Using the Labconco Rapid-Still II:

7.1 Turn the distiller on. Check that the boiling flask (visible through the open slot) is at least three-quarters full. If not, add water by setting the swing arm to the "fill" position and turning the valve on the wall. Add the water slowly! This is most important when the boiling flask contains boiling water. After filling, turn off the water valve and return the swing arm to the standby position.

NOTE: when adding water to the boiling flask, there should be no sample distillation vessel in place. A vacuum can develop that will draw sample up into the steam tubing.

7.2 Pre-clean both distillers by distilling 100 ml of 1:1 DI water and Neutralization Reagent. Collect approximately 200 ml distillate. Repeat.

7.3 Add 100 ml DI water to each digestate. Swirl to mix.

7.4 Immediately prior to distillation, slowly pour (20 ml for liquid samples and 50 mls for solid samples) Neutralization Reagent down the side of the tilted flask.

Caution: This can splatter and bump- be very careful. DO NOT MIX. Place the flask in the distillation unit and begin distillation.

Collect 300 ml distillate into a 500 ml Erylnmeyer catch flask containing 30 ml Boric Acid Solution. Make sure the glass condenser table is below the level of the Boric Acid to prevent the loss of any distilled ammonia.

8.0 Nesslerization Procedure:

8.1 Prepare an external standard curve using the 2 mg/l working standard (3.f):

Blank	50 ml DI Water
0.08 mg/l	2 ml of 2 mg/l standard + DI Water to 50 ml
0.2 mg/l	5 ml of 2 mg/l standard + DI Water to 50 ml
0.4 mg/l	10 ml of 2 mg/l standard + DI Water to 50 ml
0.8 mg/l	20 ml of 2 mg/l standard + DI Water to 50 ml
1.2 mg/l	30 ml of 2 mg/l standard + DI Water to 50 ml
1.6 mg/l	40 ml of 2 mg/l standard + DI Water to 50 ml
2.0 mg/l	50 ml of 2 mg/l standard

8.2 ICV/CCV and ICB/CCB:

Calibration verification standards (ICV/CCV): 1 ml 20 mg/l NH_3-N standard (3.g) plus DI water to 50 ml. True value equals 0.4 mg/l.

Calibration Blanks (ICB/CCB): 50 ml DI water.

8.3 Add 2 mls Nessler Reagent to each standard or distillate. Mix thoroughly and allow color to develop for 15 minutes.

8.4 Read % T at 425 nm using a 2 cm cuvette. Plot mg/l concentration against log %T.

8.5 Distillates exceeding the upper limit of the standard curve must be diluted and re-analyzed (on the spectrophotometer only- do not redistill). Dilutions should be prepared so as to fall in the top half of the curve.

9.0 Calculations:

9.1 for Liquid samples mg/l = $NH_3\text{-}N/l_{distillate} \times \frac{\text{distillate volume (ml)}}{\text{sample volume (ml)}}$

9.2 for Solid samples mg/kg as rec = $NH_3\text{-}N/l_{distillate} \times \frac{\text{distillate volume (ml)}}{\text{sample volume (g)}}$

Remember solid samples are to be corrected for % solids and reported on a dry weight basis.

9.0 Quality Control

9.1 The standard curve must contain at least 6 points and have a regression of -0.995 or better.

9.2 Immediately following the standard curve, and ICV and ICB must be analyzed. The ICV must fall within 90-110 % recovery and is read directly from the curve. The ICB must be less than 0.04 mg/l.

CCV's and CCB's have the same control limits as stated for the ICV and ICB.

9.3 Every batch of digested samples must contain a blank (PBW) and two Laboratory Control Samples (LCS's). The same LCS will be used but one will be diluted tofall in the lower half of the curve, while the other will be prepared to fall in the upper half. The PBW must be less than the detection limit. The LCS's must fall within 85-115 % recovery.

9.4 A duplicate and a matrix spike should be analyzed with each digestion batch. The matrix spike recovery should be between 75-125%. The replicate analysis should have an RPD <20%.

APPENDIX A-8

STANDARD OPERATING PROCEDURE FOR NITRATE/NITRITE-N METHOD

Nitrate/Nitrite-N Method No: 353.2
Using the Alpkem RFA 300 Analyzer

Approvals and Signatures

QA Manager: Kim B. Watson Date: 7/3/97

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1.0 Scope and Application

1.1 This method pertains to the determination of nitrite and nitrate combined in surface and saline waters, and domestic and industrial wastes. A DIH_2O extraction makes this method applicable to soils as well. The applicable range of this method is 0.05 to 10.0 mg/L nitrate-nitrite nitrogen for waters and 0.05 mg/kg to 10.0 mg/kg for soils. The range may be extended with sample dilution.

1.2 Detection Limit: 0.01 mg/L for liquids or 0.01 mg/kg for soils.

2.0 Summary of Method

2.1 A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically.

3.0 Sample Handling and Preservation

3.1 Collect a minimum of 100 mL of liquid sample or a minimum of 50 grams of soil in a plastic or glass container.

3.2 Liquid samples are preserved to pH <2 with H_2SO_4 and cooled to 4°C at the time of collection.

3.3 Holding time is 28 days from sample collection.

4.0 Standards and Reagents

All reagents and solvents used during analysis are of appropriate purity and prior to use will be checked for contamination and documented in the standard preparation logbook. A unique identifier will be assigned to each original stock material and to each subsequent dilution. The preparation logbook will include the prepared concentration and unique identifier of the prepared material, the dates of preparation and expiration, the amount and the lot numbers or unique identifiers of the materials and solvents used to prepare the material, and the identity of the person who prepared the materials. Assigned expiration dates for purchased materials must not exceed the manufacturer's expiration date. Expiration dates for laboratory prepared standards and QC materials must no exceed the shelf life allowed by the referenced analytical method, if provided.

4.1 1000 ppm Nitrate Stock

7.2187 g KNO3 dried at 105 °C plus DI water to one liter and preserved with 2 mL of chloroform.

4.2 <u>100 ppm Nitrate Intermediate</u>

10 mL of 1000 ppm Nitrate stock diluted to 100 mL with DI water.

4.3 <u>100 ppm Nitrite Stock</u>

0.4928 g $NaNO_2$ plus DI Water to approximately 900 mL. Add 2 mL chloroform (as preservative) and bring to one liter with DI Water. Store in the refrigerator.

4.4 <u>0.5 ppm Nitrite Working Standard</u>

5 mL 100 ppm Nitrite Stock plus DIH_2O to one liter.

4.5 Stock NH_4Cl- EDTA Buffer

85 g NH_4Cl and 0.1 g EDTA dissolved in 900 mL of DI water. Adjust pH to 8.5 with NH_4OH and dilute to one liter with DI water.

4.6 Working NH_4Cl - EDTA Buffer

200 mL of stock buffer plus 4 drops of Brij. Shake well.

4.7 Sulfanilamide Reagent

10.0 g SAN dissolved into 100 mL of HCl and 700 mL of DI water. Dilute to one liter with DI water and 2 drops of Brij.

4.8 NED Reagent

1.0 g N(1-naphthyl)-etheylene diamine dihydrochloride plus DI Water to one liter. Store refrigerated in amber glass bottle.

4.9 Standard Curve and Check Standard

Standard Curve:

Blank	DI water
0.02 mg/L	2 mL of 100 ppm NO3 stock plus DI water to 100 mL
0.05 mg/L	5 mL of 100 ppm NO3 stock plus DI water to 100 mL
0.10 mg/L	10 mL of 100 ppm NO3 stock plus DI water to 100 mL
0.15 mg/L	15 mL of 100 ppm NO3 stock plus DI water to 100 mL
0.20 mg/L	20 mL of 100 ppm NO3 stock plus DI water to 100 mL

Note: The curve must be run in descending order (0.20 → 0)

Check Standard:

Purchased from a commercial vendor- refer to current Lot # for true value.

4.10 Sync .20 mg/L NO_2

20 mL of 0.5 ppm Nitrite Stock plus DI water to 50 mL. Must be made fresh every day.

5.0 Procedure

5.1 Soil sample prep: weigh out 10 gram ±1 g of soil into a tared 50 mL centrifuge tube. Add **equal** amount of DI water. Shake vigorously for 15 minutes then centrifuge. If necessary, filter through a 0.45 μ filter. Analyze as liquid sample.

5.2 Turn on monitor and components from left to right (three switches). Connect appropriate pump tubes according to Figure 1, being sure to place pump tubes of similar size under same platen. Do not connect cadmium reducing column at this time.

At main menu select "instrument set up" (F9). Place "X" in appropriate column to match analysis you are performing i.e., 1(NO_2), 2(C1), 3(SO_4) then escape and select "Display Analog Signal" (F5) and by using arrow keys move down to corresponding position #1, 2 or 3 and hit "space bar".

5.3 Once all pump tubes are in place, with reagent lines in DIH_2O plus brij, close platens and instrument will begin pumping. After several minutes and after you are sure things are hooked up correctly, place reagent lines in their correct reagents and after reagents have been pumping several minutes, place cadmium coil in line taking care not to introduce air into the system.

5.4 At main menu select "Display Analog Signal" (F5), by using the function keys. Then select "Start Display" (F3). this allows you to view baseline. Once you are sure all reagents are pumping through the system, turn center knob on photometer (#305A) all the way to the right (labeled "sample"). then using knob labeled "sample", adjust until 5 + 0.1 appears in display window. Turn center knob to "Reference" and adjust to 5 + 0.1 using the "Reference" knob. After these steps, turn center knob back to "Absorbance" at which time 0.2 + should appear in display window. If not, adjust "Reference" knob up or down until it does so.

5.5 While still viewing baseline, set-up sample tray according to bench sheet (see Figure 2). Place an aliquot of liquid sample into the 2 mL sample cup. Remember that curve

must be run high to low concentration. After every 10 samples, run a CCV and CCB. If you are running a dilution, make sure that it corresponds to the correct sample. Place SYNC (0.2 ppm NO2 Std) at end of run to verify column efficiency. The column efficiency must be 96%-104%, or recondition column according to Addendum A.

5.6 Escape from "Display Analog Signal" (hit ESC key twice), then go into "Sample Table" by using Function Key (F4) and enter benchsheet, again being careful to enter correct dilutions, if any.

Once you are satisfied that it is correct, save it to file by hitting "ALT" "S" simultaneously and enter in "NO_3" along with the run date (i.e.; NO3120"A" for first run, "B" for second run, etc.) then escape back to main menu.

5.7 Return to "Display Analog Signal". As you watch for a steady baseline, set "sample wash" time to 25 seconds, "sample time" to 25 seconds and "stop count" to the number of positions filled on sample tray. Once you are sure all is correct hit "Reset". Flow rate: 2 mL sample cup, 226 uL/min for 25 seconds.

5.8 Synchronize module with 0.2 ppm NO_2 standard to reach a response of 80% of full scale by setting "Stop Count" to one and running high standard at least three times. (Reset after each time you run standard, then position the tray for position one again). Adjust peak height to 90% of full scale by using standard calibration dial located on upper left of photometer. Allow system to go back to baseline.

5.9 When you are satisfied with baseline and it appears to be steady, escape from analog signal once. Hit "ALT" "one" simultaneously then enter. When looking at top right of monitor, you wee the channel "G1", turn on, then hit start button on auto sampler. Now hit F3 and you will be able to see peaks come out as the samples/STDS are run. Run is over when the autosampler beeps. At this time you may hit "reset", but do not turn Off channel until last sample is run.

When you are sure all samples have been run and baseline has returned, escape once and hit "ALT" "1" simultaneously. This turns off the channel.

6.0 Calculating Results

6.1 Escape back to main menu. Select function key "Calculations" (F8) then select function key "Calculations" (F8) again. "enter" through what appears on screen (3

times); peaks will be displayed. Select function key (F9) "continue". Remove any points from curve if not satisfied with correlation by selecting "edit" (F3) and using arrow keys to reach point or points you wish to eliminate. Once on point you wish to eliminate, select function key "Delete" (F2). Escape once an select function key "recalculate" (F8). You may repeat the process over again if not satisfied with the correlation. Once satisfied, select function key "continue" (F9), review data to see that all QC works and then "print report" (F2).

6.2 Review data and rerun samples that need to be diluted (higher than highest point on calibration), taking care to dilute samples so they have a concentration within the top half of your curve. Dilution prep; samples are prepared for dilutions in volumetric flasks (ex: 5 mL - 50 mL = 10 fold dilution). Cadmium column must be reconditioned and all samples rerun if 0.2 ppm NO2 STD at beginning (SYNC) or at end of run is not 96%-104% efficient.

7.0 Trouble Shooting

7.1 If unsteady baseline, check to make sure all reagents are in respective reagents, or change pump tubes that are worn. Filter reagents through 0.45 um membrane filter. If broken bubble pattern is seen exiting the cadmium column, (where they look good entering the column), the column may be badly pitted and in need of replacement.

8.0 Quality Control

8.1 An ICV/ICB are analyzed prior to any samples. The ICV must be within the control limits of 90-110%. The ICB must be less than the reporting limit of 0.01 mg/L.

8.2 A CCV/CCB are analyzed every 10 samples. The CCV must be within the control limits of 90-110%. The CCB must be less than the reporting limit of 0.01 mg/L.

8.3 A matrix spike/replicate are analyzed with every batch of samples. The control limits for the matrix spike is 75-125%. The control limit for the replicate is <20%.

References

1. USEPA EMSLV Method 353.2, Determination of Nitrate-Nitrite Nitrogen by Automated Colorimetry. Revision 2.0, August 1993.

wc3532.wpd

Figure 2
Table Name: Nitrate

CUP#	Sample ID	DIL	WGT	CUP#	Sample ID	DIL	WGT
1	SYNC	1	1	2	W	1	1
3	S1	1	1	4	S2	1	1
5	S3	1	1	6	S4	1	1
7	S5	1	1	8	S6	1	1
9	W	1	1	10	ICV ERA	1	1
11	ICB	1	1	12	PBW	1	1
13		20	1	14		1	1
15		1	1	16		1	1
17		1	1	18		1	1
19		1	1	20		1	1
21		1	1	22		1	1
23	CCB	1	1	24		1	1
25		1	1	26		1	1
27		1	1	28		1	1
29		1	1	30		1	1
31		1	1	32		1	1
33		1	1	34	CCV ERA	1	1
35	CCB	1	1	36		1	1
37		1	1	38		1	1
39		1	1	40		1	1
41		1	1	42		1	1
43		1	1	44		1	1
45	0.02 ppmNO_2	1	1	46	CCV ERA	1	1
47	CCB	1	1	48		1	1

Addendum A

OTCR Activation (Cadmium Column)

a. Detach one sleeve from the heavy walled polyethylene tubing.

b. Using a 10 cc plastic syringe, flush the OTCR with the described solutions using the following procedure:

1. Deionized Water

2. 0.5 N Hydrochloric Acid

The hydrochloric acid may cause pitting of the cadmium reactor interior surface if left in the OTCR for longer than a few minutes.

3. Deionized Water

After the HCl slush, quickly rinse with deionized water.

4. 2% Copper Sulfate

Slowly flush the OTCR with 10 cc of 2% copper sulfate. Repeat. Precipitated copper may be observed exiting the reactor.

5. Deionized Water

Flush with deionized water until no more precipitated copper is flushed from the reactor. This requires a fairly vigorous flush. Repeat 2-3 times.

6. Ammonium Chloride/EDTA Buffer

Fill the OTCR with Stock buffer. The reactor should be stored with Stock buffer when not in use.

NOTE: Do not introduce air into the cadmium tube during this process.

APPENDIX A-9

STANDARD OPERATING PROCEDURE FOR NITRITE-N

Nitrite-N SOP
Method No. 354.1

Approvals and Signatures

QA Officer: Martha Roy Date: 3/20/97

Inorganic Section Head: Kristene Aubin Date: 3/20/97

1.0 Scope and Application

1.1 This method is applicable to the determination of nitrite in drinking, surface and saline waters, domestic and industrial wastes.

1.2 The method is applicable in the range from 0.01 to 1.0 mg NO_2-N/L.

1.3 The reporting limit for this method is 0.005 mg/L.

2.0 Summary of Method

2.1 The diazonium compound formed by diazotation of sulfanilamide by nitrite in water under acid conditions is coupled with N-(1-naphthyl) ethylenediamine dihydrochloride to produce a reddish-purple color which is read in a spectrophotometer at 543 nm.

3.0 Sample Handling and Preservation

3.1 A minimum sample volume of 100 mLs is collected in non-preserved plastic or glass containers.

3.2 Store samples at 4 ±2°C until analysis. Samples must be analyzed within 48 hours of collection.

4.0 Reagents:

4.1 100 mg/L Nitrite-N Stock:

0.4928 g $NaNO_2$ plus DI Water to approximately 900 mL. Add 1 mL chloroform (as preservative) and bring to one liter with DI Water. Store in the refrigerator.

4.2 0.5 mg/L Working Standard:

PREPARE FRESH DAILY. 5 mL 100 mg/L stock plus DI Water to one liter.

4.3 50 mg/L Nitrite-N Check Standard Stock:

0.2464 g $NaNO_2$ plus DI Water to approximately 500 mL. Add 1 mL chloroform (as preservative) and bring to one liter with DI Water. Be sure to use the Sodium Nitrite reserved for check standards.

4.4 0.25 mg/L Working Check Standard:

5 mL 50 mg/L Check Standard Stock plus DI Water to one liter.

4.5 Sulfanilamide Reagent:

Dissolve 5.0 grams sulfanilamide in approximately 200 mL DI Water with 50 mL conc. HCl. Bring to 500 mL with DI Water. Store refrigerated in amber glass bottle.

4.6 NED Reagent:

1.0 g N(1-naphthyl)-etheylene diamine dihydrochloride plus DI Water to one liter. Store refrigerated in amber glass bottle.

4.7 Standard Curve:

Blank	50 mL DI H2O
0.005 mg/L Std.	0.5 mL 0.5 mg/L Working Std plus DI Water to 50 mL
0.01 mg/L Std.	1.0 mL 0.5 mg/L Working Std plus DI Water to 50 mL
0.02 mg/L Std.	2.0 mL 0.5 mg/L Working Std plus DI Water to 50 mL
0.05 mg/L Std.	5.0 mL 0.5 mg/L Working Std plus DI Water to 50 mL

0.10 mg/L Std.	10.0 mL 0.5 mg/L Working Std plus DI Water to 50 mL
0.15 mg/L Std.	15.0 mL 0.5 mg/L Working Std plus DI Water to 50 mL
0.20 mg/L Std.	20.0 mL 0.5 mg/L Working Std plus DI Water to 50 mL

5.0 Analysis:

5.1 All glassware must be rinsed with DI Water.

5.2 Use pH paper to check that pH is not greater than 10. If necessary, adjust to approximately pH 6 with 10% HCL.

5.3 All samples must be filtered. Use 50 mL sample, or a dilution of sample if known to be high.

5.4 Add 1 mL Sulfanilamide. **Note- This reagent must be added first.**

5.5 Add 1 mL NED reagent. Stopper and mix thoroughly.

5.6 Allow color to develop for 15 minutes then read %T 543 nm. For low level samples, use a 2 cm cuvette and do not use the 0.15 and 0.20 mg/L Standards.

For high level samples, use a 1 cm cell, and read the entire curve.

6.0 Calculations:

Plot concentration (in mg/L) against log %T 543 nm. Any sample which exceeds the standard curve must be diluted and reanalyzed.

7.0 Quality Control:

7.1 For nitrite calibration blanks and verification standards are analyzed at a frequency of 10%. The calibration blanks must be less than the reporting limit of 0.005 mg/L and the verification standards must have a recovery of between 90-110%.

7.2 A replicate analysis is performed per batch of 20 samples and a matrix spike analysis is also performed at the same frequency. The replicate analysis should have an RPD of <20%, and the matrix spike recovery should be between 75-125%.

APPENDIX A-10

STANDARD OPERATING PROCEDURE FOR PHOSPHATE AS P

Phosphate as P
Method 365.2:TOTL

Approvals and Signatures

QA Officer: Martha Roy Date: 1/22/97

Wet Chemistry Section Head: David E. Meadows Date: 01/22/97

1.0 Scope and Application

1.1 This method covers the determination of orthophosphate in aqueous samples. The method may be modified to perform phosphate analysis on soils.

1.2 The method is based on the reactions that are specific for the orthophosphate ion.

1.3 The reporting limit for this method is 0.01 mg/L
solids/soils - 2 mg/Kg on an "as received" basis.

2.0 Summary of Method

2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

2.2 Organic phosphorus compounds are converted to the orthophosphate form by persulfate digestion. Only orthophosphate forms a blue color in this test.

3.0 Sample Handling and Preservation

3.1 A minimum of 100 mL of sample must be collected in H_2SO_4 preserved plastic or glass containers. The samples must be preserved to a pH < 2.

3.2 The sample must be cooled to 4 ± 2°C, and be analyzed within 28 days of

collection.

4.0 Standards and Reagents

All prepared standards and reagents are assigned an expiration date of six (6) months from the date of preparation; unless the expiration date of the parent solution expires sooner than that expiration date is used. All standards and reagents are stored at room temperature unless otherwise noted. The preparation of all standards is recorded in the wet chemistry standard preparation notebook.

4.1 50 mg/L PO_4-P Stock:

0.2195 g KH_2PO_4 plus DI water to one liter.

4.2 1.0 mg/L PO_4-P Stock:

20 mL 50 mg/L stock plus DI water to one liter.

4.3 30% H_2SO_4 Solution:

Slowly and carefully add 600 mL conc H_2SO_4 to approximately 1200 mL DI water. Bring to 2 liters with DI water. Cool before using.

4.4 Phenolphthalein Indicator:

Approximately one gram Phenolphthalein in 100 mL Isopropyl Alcohol.

4.5 Saturated Base:

1000 g NaOH pellets dissolved in 1000 mL DI water. Allow to cool before using.

4.6 1 N H_2SO_4:

28 mL (51.4 g) conc. H_2SO_4 slowly added to approximately 900 mL DI water. Bring to 1 liter with DI water.

4.7 5 N H2SO4:

140 mL (257 g) conc. H_2SO_4 slowly added to approximately 700 mL DI water.

Bring to 1 liter with DI water.

4.8 Ammonia Molybdate Reagent:

20.0 g $(NH_4)6Mo_7O_{24}.4H_2O$ plus DI water to 500 mL. Refrigerate.

4.9 Antimony Potassium Tartrate Reagent:

1.3715 g $K(SbO)C_4HrO_6$ ½ H_2O plus DI water to 500 mL. Store refrigerated in an amber glass bottle.

4.10 Combined Color Reagent:

60 mL DI water
30 mL Ammonium Molybdate Reagent
10 mL Antimony Potassium Tartrate Reagent
100 mL 5 N H2SO4
1.06 g Ascorbic Acid - crystals or powder

Mix until all Ascorbic Acid is dissolved. Can be used for 2-3 hours and will treat 24 standards or samples.

4.11 Standard Curves: Prepare the following seven (7) point calibration curve in the following manner.

mLs of 1 mg/L Phosphate standard used	mLs of DI water used	Final curve concentration (mg/L)
---	100	0 (Blank)
1.0	99.0	0.01
2.0	98.0	0.02
5.0	95.0	0.05
10.0	90.0	0.1
30.0	70.0	0.3
70.0	30.0	0.7

5.0 Procedures

5.1 All glassware must be rinsed with 10% HCl, followed by several rinses with DI water.

A series of 250 mL Erlenmeyer flasks, reserved for phosphate analysis only, is stored with HCl/DI water. These are covered with 100 mL plastic tri-corner beakers; which may be rinsed with the contents of the flasks. Flasks and beakers should then be rinsed with DI water.

Following analysis, the Erlenmeyer flasks should be thoroughly rinsed with DI water, filled to 200 mL with DI water, then filled to the brim with 10% HCl. Cover with clean tri-corner beakers.

5.2 Samples: Most samples will be preserved with H_2SO_4, although some may not. All liquid samples must be thoroughly mixed before removing an aliquot for analysis. This is very important! Prior to analysis, check that pH <2 and record on the benchsheet.

5.3 Unless a sample is known to be high, pipet 100 mL into appropriate Erlenmeyer flask. If a dilution is required, pipet sample and bring to 100 mL with DI water.

5.4 Soils and other solid samples: accurately weight 0.5 grams directly into flask and add DI water to 100 mL.

5.5 To all blanks, standards and samples, add 2 mL 30% H2SO4 and one scoop (0.3 grams) Potassium Persulfate. Swirl to mix. For soil and solid samples, add 10 mL 30% H_2SO_4 and 5 scoops (1.5 grams) Potassium Persulfate. Swirl to mix.

5.6 Place flasks on hot plates (under fume hood) and adjust to maximum heat. Allow samples to boil and evaporate until the volume is below 50 mL, then remove from heat. Watch for bumping or samples that splatter. These samples may need to be digested separately so they do not contaminate or crack other flasks. This is especially true for soils samples.

5.7 The digestion should take approximately one hour. There is no harm in allowing a sample to digest to well below 50 mL. However, under no circumstances should a sample be allowed to reach dryness.

5.8 Briefly rinse down the inner surface of the flask and allow the digested sample to cool.

5.9 Digested samples, especially soils, are very acidic and need to be neutralized. Add 2-3 drops of phenolphthalein indicator solution (add more if needed for strongly colored samples) followed by saturated NaOH dropwise until a permanent pink color develops. Add 1N H_2SO_4 dropwise until the pink color disappears, then add one more drop.

5.10 Rinse down the sides of the flask and swirl to mix. Soil samples may turn pink again slowly, requiring the addition of more one N H_2SO_4.

Pour sample into 100 mL graduated cylinder and bring to 100 mL with DI water. Pour back into flask and swirl to mix.

Pour 50 mL into graduated cylinder and transfer this to the appropriately numbered tri-corner beaker. You should now have an Erlenmeyer flask and a tri-corner beaker, each with the same number and each containing 50 mL of neutralized digestate.

For soil samples, it can be helpful to pour off 90 mL of digestate into the tri-corner beaker leaving only 10 mL in the Erlenmeyer. Adding 40 mL DI water to the flask gives a five-fold dilution and will most likely save you from many dilutions later on.

5.11 Add 8 mL Combined Color Reagent to each Erlenmeyer and swirl to mix. Allow color to develop for 15 minutes and read percent T 650 nm using a 5 cm cuvette for low level and a 2 cm cuvette for high level analysis.

All soil samples and any liquid sample exhibiting any turbidity or particulates must be filtered prior to reading on the spectrophotometer.

Any sample which exceeds the standard curve must be diluted and recolorized. the digestate may be diluted up to one hundred fold. Should the digestate require greater dilution, the possibility exists that the acid and persulfate were exhausted

before complete digestion occurred and the sample must be redigested using a smaller aliquot.

6.0 Calculations

Plot concentration (mg/L) against Log percent T 650 nm. Appropriate dilutions must be made for any sample that exceeds the standard curve.

7.0 Quality Control

7.1 Calibration blanks and verification standards are analyzed at a frequency of 10%. The calibration blanks must be less than the reporting limit of 0.01 mg/L and the verification standards must have a recovery of between 90-110%. The verification is purchased commercially - true value varies with each lot.

7.2 A Laboratory Control Sample (LCS) is performed per batch of 20 samples of the same matrix. The LCS must be within the control limit of ± 20% or the samples prepared in that batch must be reprepared and reanalyzed.

7.3 A replicate analysis is performed per batch of 20 samples and a matrix spike analysis is also performed at the same frequency. The replicate analysis should have an RPD of ± 20%, and the matrix spike recovery should be between 75-125%. The matrix spike recovery is calculated with the following equation:

$$MS\ Recovery\ (\%) = \frac{SSR - SR}{SA} * 100$$

where:
SSR = Spike Sample Results
SR = Sample Results
SA = Spike Added (concentration)

The Relative Percent Difference (%RPD) between the sample and replicate analysis is calculated with the following equation:

$$\% RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} * 100$$

where:
RPD = Relative Percent Difference
D_1 = First Sample Value
D_2 = Second Sample Value (duplicate)

APPENDIX A-11

STANDARD OPERATING PROCEDURE FOR ORTHOPHOSPHATE AS P

Orthophosphate as P
Methods 365.2:ORTH

Approvals and Signatures

QA Officer: Martha Roy Date: 1/22/97

Wet Chemistry Section Head: David E. Needham Date: 01/22/97

1.0 Scope and Application

1.1 This method covers the determination of orthophosphate in aqueous samples.

1.2 The method is based on the reactions that are specific for the orthophosphate ion.

1.3 The reporting limit for this method is 0.01 mg/L

2.0 Summary of Method

2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

2.2 Only orthophosphate forms a blue color in this test.

3.0 Sample Handling and Preservation

3.1 A minimum of 100 mLs of sample must be collected in non preserved plastic or glass containers.

3.2 The sample must be cooled to 4 ± 2°C, and be analyzed within 48 hours of collection.

4.0 Standards and Reagents

All prepared standards and reagents are assigned an expiration date of six (6) months from the date of preparation; unless the expiration date of the parent solution expires sooner than that expiration date is used. All standards and reagents are stored at room temperature unless otherwise noted. The preparation of all standards is recorded in the wet chemistry standard preparation notebook.

4.1 50 mg/L PO_4-P Stock:

0.2195 g KH_2PO_4 plus DI water to one liter.

4.2 1.0 mg/L PO_4-P Stock:

20 mL 50 mg/L stock plus DI water to one liter.

4.3 Ammonium Molybdate Reagent:

20.0 g $(NH_4)_6Mo_7O_{24}$ 4 H_2O plus DI water to 500 mL. Refrigerate.

4.4 Antimony Potassium Tartrate Reagent:

1.3715 g $K(SbO)C_4H_4O_6$ 1/2 water plus DI water to 500 mL. Store refrigerated in amber glass bottle.

4.5 5 N H2SO4 Solution:

140 mL (257g) conc H_2SO_4 slowly add to approximately 700 mL DI water. Bring to one liter with ID water. Cool before using.

4.6 Combined Color Reagent:
60 mL DI water
30 mL Ammonium Molybdate Reagent
10 mL Antimony Potassium Tartrate Reagent
100 mL 5 N H_2SO_4
1.06 g Ascorbic Acid - crystals or powder

Mix until all Ascorbic Acid is dissolved. This should be used within 2-3 hours and will treat 24 standards or samples.

4.7 Standard Curves: Prepare the following seven (7) point calibration curve in the following manner.

mLs of 1 mg/L Phosphate standard used	mLs of DI water used	Final curve concentration (mg/L)
---	100	0 (Blank)
1.0	99.0	0.01
2.0	98.0	0.02
5.0	95.0	0.05
10.0	90.0	0.1
30.0	70.0	0.3
70.0	30.0	0.7

Mix Standards and transfer 50 mL to new, clean 100 mL volumetric flask.

5.0 Procedure

5.1 All glassware must be rinsed with 10% HCl, followed by several rinses of DI water.

5.2 Samples must not be preserved, and must be allowed to reach room temperature prior to analysis.

5.3 Unless the sample is absolutely clear and free of particulates, filter through an HCl rinsed/DI water rinsed 0.45 um filter.

5.4 Pipette 50 mL of filtered sample into clear 100 mL volumetric flask.

5.5 Add 8 mL Combined Color Reagent to each blank, standard and sample. Mix and allow color to develop for 15 minutes. Read percent T 650 nm, using a 5 cm cuvette for low-level and a 2 cm cuvette for high level analysis.

6.0 Calculations

Plot concentration (mg/L) against Log percent T 650 nm. Appropriate dilutions must be made for any sample that exceeds the standard curve.

7.0 Quality Control

7.1 Calibration blanks and verification standards are analyzed at a frequency of 10%. The calibration blanks must be less than the reporting limit of 0.01 mg/L and the verification standards must have a recovery of between 90-110%. The verification is purchased commercially - true value varies with each lot.

7.2 A Laboratory Control Sample (LCS) is performed per batch of 20 samples of the same matrix. The LCS must be within the control limit of ± 20% or the samples prepared in that batch must be reprepared and reanalyzed.

7.3 A replicate analysis is performed per batch of 20 samples and a matrix spike analysis is also performed at the same frequency. The replicate analysis should have an RPD of ± 20%, and the matrix spike recovery should be between 75-125%. The matrix spike recovery is calculated with the following equation:

$$MS\ Recovery\ (\%) = \frac{SSR - SR}{SA} * 100$$

where:
SSR = Spike Sample Results
SR = Sample Results
SA = Spike Added (concentration)

The Relative Percent Difference (%RPD) between the sample and replicate analysis is calculated with the following equation:

$$\% RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} * 100$$

where:
RPD = Relative Percent Difference
D_1 = First Sample Value
D_2 = Second Sample Value (duplicate)

APPENDIX A-12

STANDARD OPERATING PROCEDURE FOR SULFIDE (METHOD 376.2/4500-S^2-D)

Sulfide
Method 376.2/4500-S^2-D

Approvals and Signatures

QA Officer: Martha Boy Date: 8/14/95

Wet Chemistry Manager: [illegible] Date: 14 Aug 95

1.0 Scope and Application

1.1 This method is applicable to the measurement of total and dissolved sulfides in drinking, surface and saline waters, domestic and industrial wastes.

1.2 Acid insoluble sulfides are not measured by this method. Copper sulfide is the only common sulfide in this class.

1.3 The method is suitable for the measurement of sulfide in concentrations up to 20 mg/L.

2.0 Summary of Method

2.1 Sulfide reacts with dimethyl-p-phenylenediamine (p-aminodimethylaniline) in the presence of ferric chloride to produce methylene blue, a dye which is then measured spectrophotometrically.

2.2 Detection limit for 50 ml sample is 0.02 mg/l.

3.0 Sample Handling and Preservation

3.1 Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an unmeasurable form. Dissolved oxygen should not be present in any water used to dilute standards.

3.2 A minimum volume of 50 mls of sample must be collected in plastic or glass bottles. The sample must be preserved with zinc acetate plus NaOH to pH >9.

The sample must remain at 4 ° C.

3.3 Sample must be analyzed within 7 days of collection.

4.0 Reagents

4.1 Amine Sulfuric Acid

First prepare a stock solution, dissolving 13.5 gram N,N-dimethyl-p-phenylenediamine oxalate in a cold mixture of 25 ml concentrated H_2SO4 and 10 ml DIH_2O. Cool and dilute to 50 ml with DIH_2O.

Now dilute 25 ml of this stock solution with 975 ml 1 + 1 H_2SO4. Store refrigerated in an amber glass bottle.

4.2 Ferric Chloride Solution

Dissolve 100 grams $FeCl_3.6H_2O$ in 40 ml DIH_2O.

4.3 Diammonium Hydrogen Phosphate Reagent

Dissolve 50 grams $(NH_4)2HPO_4$ in 100 ml DIH_2O.

4.4 Preparation of Sulfide Stock For Standard Curve:

- small crystal (preferably <0.5 g) $Na_2S.9H_2O$ in tri-corner beaker. Rinse 3 times with DIH_2O. Dry crystal thoroughly with kimwipes.
- weigh crystal to 0.1 mg and dissolve in 500 ml DIH2O.

$$Concentration\,stock\ \frac{mg}{L} = \frac{(crystal\,wgt)\,(0.1335^{*})\,(1000\frac{mg}{g})}{0.51}$$

(*0.1335→ $Na_2S.9H_2O$ = 13.35 % S)

Note: The stock should be approximately 20-70 mg/l.

4.5 Preparation of Intermediate Stock

- The intermediate stock should be between 1-5 mg/l.
- usually a 10 →100 ml or 5→ 100 ml dilution will bring your stock into the proper range.

4.6 Standard Curve

- Blank + at least 3 standards
- Standard #1: approximately 0.05 mg/l
  Standard #2: approximately 0.1 mg/l
  Standard #3: approximately 0.2 mg/l

Note: Add more points to the curve as needed.

- All blanks, standards and samples in 50 ml volumetric flask.

5.0 Procedure

5.1 Samples are preserved with NaOH and zinc acetate which forms zinc sulfide. This is a precipitate which tends to settle on the bottom of the sample bottle. Before pouring or pipetting) sample, shake vigorously. When poured, the sample should look milky and may even have a few white flecks in it.

5.2 To 50 mL of each blank, standard and sample:

- Add 0.5 ml Amine Sulfuric Acid with 500 mL Eppendorf pipette. The milky appearance should disappear from the samples. Mix thoroughly.

Note: Amine Sulfuric Acid is kept refrigerated and is 50% H_2SO_4 - please use caution with this.

- Should the samples require filtering, do so now. Be careful to retain as much sample as possible.
- Add two drops $FeCl_3$ solution - shake, stand for one minute.
- Add 0.5 mL Diammonium Hydrogen Phosphate Reagent.

6.0 Calculations

6.1 Read percent T at 600 nm with two centimeter cell. Color intensities are fairly stable and will last at least one-half hour. Plot concentration versus Log percent T to give mg/L. Apply any applicable dilution factor.

7.0 Quality Control

7.1 An ICV/ICB and CCB/CCV are analyzed with each batch. ICV and CCV's are prepared from $NA_2S{\cdot}9H_2O$ as in 4.0, although from a separate source. The ICB/CCB's must be less than the reporting limit of 0.02 mg/l. The ICV/CCV's must be within the control limits of 90-110%.

7.2 A matrix spike and replicate analysis should be analyzed per batch. The matrix spike should have a recovery of 75-125%. The replicate should have an RPD of <20%.

7.3 Be sure to record the sources and lot numbers of the sodium sulfide used for the standard curve and the ICV/CCV.

APPENDIX A-13

STANDARD OPERATING PROCEDURE FOR SULFIDE IN SOIL

Sulfide in Soil
Based on Method 9030/IN715, Acid Soluble Sulfide

Approvals and Signatures

QA Officer: Martha E. Roy Date: 10/5/94

Wet Chemistry Manager: [illegible] Date: 3 Oct 94

1.0 Scope and Application

1.1 The distillation procedure described in this method is designed for the determination of sulfides in aqueous, solid waste materials, or effluents.

1.2 This method provides only a semi-quantitative determination of sulfide compounds considered "acid-insoluble" (e.g., CuS and SnS_2) in solid samples. Recovery has been shown to be 20 to 40% for CuS, one of the most stable and insoluble compounds, and 40 to 60% for SnS2 which is slightly more soluble.

1.3 This method is not applicable for distilling reactive sulfide, however, Method 9030 is used to quantify the concentration of sulfide from the reactivity test.

1.4 This method measures total sulfide which is usually defined as the acid-soluble fraction of a waste. If, however, one has previous knowledge of the waste and is concerned about both soluble sulfides such as H_2S, and metal sulfides, such as CuS and SnS_2, then total sulfide is defined as the combination of both acid-soluble and acid-insoluble fractions. For wastes where only metal sulfides are suspected to be present, only the acid-insoluble fraction needs to be performed.

2.0 Summary of Method

2.1 For acid-soluble sulfide samples, separation of sulfide from the sample matrix is accomplished by the addition of sulfuric acid to the sample. The sample is heated to 70 °C and the hydrogen sulfide (H_2S) which is formed is distilled under acidic conditions and carried by a nitrogen stream into zinc acetate gas scrubbing bottles

where it is precipitated as zinc sulfide.

2.2 The sulfide in the zinc sulfide precipitate is oxidized to sulfur with a known excess amount of iodine. Then the excess iodine is determined by titration with a standard solution of phenyl arsine oxide (PAO) or sodium thiosulfate until the blue iodine starch complex disappears. As the use of standard sulfide solutions is not possible because of oxidative degradation, quantitation is based on the PAO or sodium thiosulfate.

3.0 Sample Handling and Preservation

3.1 Soil samples are not preserved, but are maintained at 4° C until analysis. Holding time is seven days from sample collection.

3.2 Waste effluents and other liquid samples should be preserved with zinc acetate (2 ml/500 ml sample) and sodium hydroxide to pH >9. Holding time is seven days from collection.

4.0 Reagents

4.1 Zinc Acetate (2 N):

109.74 gram $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ plus DIH_2O to 250 ml.

4.2 Formaldehyde (37%):

Purchased commercially

4.3 Scrubber Solution:

12.5 ml 2 N Zinc Acetate, 25 ml 37% Formaldehyde plus 500 ml DIH_2O.

4.4 Sulfuric Acid (30%):

Slowly add 300 ml concentrated H_2SO_4 to 700 ml DIH_2O, stirring constantly. Allow to cool before use.

4.5 Iodine Solution (0.025 N):

Dissolve 25 gram KI in 700 ml DIH_2O. Add 3.2 gram I_2 and allow to dissolve. Bring to 1 liter with DIH_2O.

4.5.1 Standardize as follows: Dissolve approximately 2 gram KI in 150 ml DIH_2O. Add exactly 20 ml Iodine solution and mix. Bring to 200 ml with DIH_2O.

4.5.2 Titrate with 0.025 N Thiosulfate (using starch indicator, endpoint = blue to clear)

$$\text{Normality} = \frac{\text{ml Titrant x N Titrant}}{\text{mls iodine solution}}$$

4.6 Sulfide Standard

Preparation of Sulfide Stock:

a. small crystal (approximately 0.5 g) $Na_2S.9H_2O$ in tri-corner beaker. Rinse 3 times with DIH_2O. Dry crystal thoroughly with kimwipes.

b. weigh crystal to 0.1 mg and dissolve in 500 ml DIH2O.

$$\text{Concentration} = \frac{\text{(crystal wgt)(0.1335*)(1000 mg/g)}}{0.5\ \text{l}} = \text{mg/l stock}$$

(*0.1335→ $Na_2S.9H_2O$ = 13.35 % S)

The stock should be approximately 100-150 mg/l.

4.7 Thiosulfate Titrant (0.025 N)

See D.O. SOP for preparation.

5.0 Procedure

5.1 Pipette 50 mls scrubber solution into the impingers (2 for each station).

5.2 Pour 50 ml 30% H_2SO_4 into the funnel unit (be sure stopcock is closed).

5.3 Place 10 grams of soil sample into a double necked round bottom flask containing a one inch stir-bar. Rinse the neck and sides of the flask with 30-50 ml DIH_2O. For liquid samples, use 100 mls and rinse likewise.

5.4 Assemble apparatus (refer to diagram) and adjust flow rate of nitrogen gas through system to 60 ml/min. Allow system to purge with nitrogen for approximately 10 minutes. Check that all connections are tight and all impingers are bubbling.

5.5 Turn on hotplate and bring water bath to 70°C.

5.6 Slowly open the funnel stopcock and allow the 30% H_2SO_4 to mix with the sample. Watch for possible reactions such as a rapid burst of bubbles, foaming, or bumping. Be prepared to stop or slow the addition of H_2SO_4 until any reaction has subsided. It should take about two minutes to complete the H_2SO_4 transfer.

5.7 Check that temperature of the water bath is at 70°C and set timer for 90 minutes. During this time, frequently check flasks for adequate stirring and impingers for consistent nitrogen flow.

5.8 Following the 90 minute reaction time, turn off heat and nitrogen gas, and disassemble the apparatus. Check that the pH of the sample is <2.

5.9 Transfer the scrubber solution to a 100 ml volumetric flask. Using a pipette bulb, blow out any solution contained in the fritted bubbler. Rinse this tube and all internal surfaces of the impinger with DIH_2O and invert 10 times to mix.

5.10 Repeat for each impinger. Take care to label each volumetric flask with sample designation and whether it is form the "front" or "back" position.

Hydrogen Sulfide Titration:

5.11 Transfer the scrubber solution (5.9) into a 250 ml erlynmeyer flask. Add 1 ml 50% HCl and 5 ml 0.025 N Iodine solution. Should all the iodine be reduced by the sulfide present, add a second 5 ml aliquot of Iodine. If necessary continue to add Iodine in 5 ml increments until Iodine color remains. Record total volume of Iodine added. Rinse sides of flask with DIH_2O and bring volume to approximately 200 ml.

5.12 Titrate with 0.025 N Thiosulfate to a straw color. Add a squirt of starch solution and titrate from blue to clear endpoint. Record initial and final volumes of titrant.

6.0 Calculations

$$\frac{(\text{mls } I_2 \times N\ I_2) - (\text{ml titrant} \times \text{N titrant}) \times (32\ \text{gram}/2\ \text{eq.}) \times 1000}{\text{Sample g or ml}}$$

= sulfide mg/kg or mg/l.

7.0 Quality Control

7.1 A method blank, replicate and matrix spike are on each day of analysis. The blank should be less than the reporting limit of 48 mg/kg (4.8 mg/l for aqueous samples).

APPENDIX A-14

STANDARD OPERATING PROCEDURE FOR BIOLOGICAL OXYGEN DEMAND

Biological Oxygen Demand
Method 405.1

Approvals and Signatures

QA Officer: Martha Roy Date: 9/25/96

Wet Chemistry Section Head: Paul G. Meadlin Date: 9/25/96

1.0 Scope and Application

1.1 The biochemical oxygen demand (BOD) test is used for determining the relative oxygen requirements of municipal and industrial wastewaters. Application of the test to organic waste discharges allows calculation of the effect of the discharges on the oxygen resources of the receiving water.

1.2 The BOD test is an empirical bioassay-type procedure which measures the dissolved oxygen consumed by microbial life while assimilating and oxidizing the organic matter present. The standard test conditions include dark incubation at 20°C for a specified time period (often 5 days). The actual environmental conditions of temperature, biological population, water movement, sunlight, and oxygen concentration cannot be accurately reproduced in the laboratory. Results obtained must take into account the above factors when relating BOD results to stream oxygen demands.

1.3 The procedure for soil samples has been adopted from the "Procedures For Handling and Chemical Analysis of Sediment and Water Samples by Russell H. Plumb, May 1981."

1.4 The reporting limit for waters by this method is 2 mg/L and for soils 120 mg/Kg.

2.0 Summary of Method

2.1 The sample analyzed over an appropriate range of dilutions, is incubated for 5 days at 20 °C in the dark. The reduction in dissolved oxygen concentration during the

incubation period yields a measure of the biochemical oxygen demand.

3.0 Sample Handling and Preservation

3.1 A minimum sample volume of 1 liter for waters is collected in unpreserved plastic or glass containers. At least 100 grams of soil should be collected for soil samples. Samples are maintained at 4 °C and are analyzed within 48 hours of collection. Note: for composite samples, holding time is based on the beginning of the composite cycle.

4.0 Reagents

4.1 Magnesium Sulfate Solution:

42.75 gram $MgSO_4 \cdot 7H_2O$ plus DIH_2O to 1900 ml.

4.2 Calcium Chloride Solution:

69.16 gram $CaCl_2 \cdot 2H_2O$ plus DIH_2O to 1900 ml.

4.3 Ferric Chloride Solution:

0.48 gram $FeCl_3 \cdot 6H_2O$ plus DIH_2O to 1900 ml.

4.4 Phosphate Buffer Solution:

16.15 gram KH_2PO_4, 41.33 gram K_2HPO_4, 63.46 gram $Na_2HPO_4 \cdot 7H_2O$, 3.23 gram NH_4Cl plus DIH_2O to 1900 ml.

4.5 Dilution Water:

20 ml each of reagents 4.1-4.4 in carboy reserved for this purpose. Bring to 20 liters with DIH_2O. Adjust temperature to 21° C, then bubble for 30 minutes.

4.6 Polyseed:

Empty contents of one capsule into an erlynmeyer flask. Add 100 ml dilution water to flask. Stir and bubble for 1 hour then filter through Whatman 541 filter paper. 1.5 ml of this solution will result in a 5 day depletion of approximately 0.6

mg/l.

Note: Wash hands after preparing polyseed.

4.7 Glucose/Glutamic Acid:

150 mg. of glucose, 150 mg. Glutamic Acid plus DIH_2O to 1 liter.

5.0 Procedure

5.1 The pH of each sample is measured, and where needed, is adjusted to between 6 and 8. Samples are checked for the presence of chlorine. When found it is neutralized with sodium sulfite.

5.2 A series of dilutions is prepared for each sample; the exact range depending on sample type, prior history and other factors. When the sample is to comprise 50% or more, it is brought to 21°C and bubbled for four minutes prior to aliquoting.

5.3 Each incubation bottle is seeded with 1.5 ml (0.5%) polyseed and filled with dilution water.

5.4 Two D.O. meters are calibrated by comparison with the modified Winkler Method*, and the initial dissolved oxygen concentrations are measured and recorded.

* Refer to Dissolved Oxygen SOP

5.5 Bottles are stoppered and covered with a plastic cap. Check that there is no air trapped in BOD bottle, and that there is water displaced above the stopper. All bottles are then incubated, at 20° C for 5 days. On day 5 the final dissolved oxygen concentration is measured and recorded.

5.6 For soil samples, weigh 3-5 gram of well mixed sample into a BOD bottle. Seed as a liquid, fill with dilution water. Read initial and final BOD.

6.0 Calculation

6.1 Seed correction is determined by triplicate analysis of 0.5% polyseed. The average seed depletion is then subtracted from the net depletion from each dilution.

6.2 The oxygen depletion over five days is calculated for each bottle, with the Seed contribution being subtracted out. Corrected oxygen depletion should fall between 2 and 6 mg/L.

6.3 Calculate as below:

Liquid Samples:

$$mg/L = \frac{net\ depletion\ -\ seed\ depletion}{\%\ sample\ /\ 100\%}$$

Soil Samples:

$$mg/Kg = \frac{(net\ depletion\ -\ seed\ depletion)\ *\ 300\ mL}{sample\ mass\ (g)}$$

7.0 Quality Control

7.1 The oxygen depletion over five days in the unseeded blank should not exceed 0.2 mg/L.

7.2 A standard preparation of glucose and glutamic acid (150 mg of each per liter - BOD = 200 mg/L) and an independent Laboratory Control Sample are included in each analysis.

7.3 Provided sufficient sample volume is provided, one replicate and matrix spike analysis is performed per 20 samples. The replicate analysis should have an RPD <20%. The matrix spike recovery should be between 75-125%.

APPENDIX A-15

STANDARD OPERATING PROCEDURE FOR TOTAL ORGANIC CARBON

Total Organic Carbon
Method 415.1

Approvals and Signatures

QA Manager: Martha Roy Date: 6/23/97

Inorganics Section Head: Kristine L. Auler Date: 6/23/97

1.0 Scope and Application

1.1 This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes.

1.2 Detection Limit: 0.5 mg/L

Note: Lower detection limits are possible and may be negotiated on a case by case basis.

2.0 Summary of Method

2.1 Organic carbon in a sample is converted to carbon dioxide (CO_2) by wet chemical oxidation. The CO_2 formed is measured directly by an infrared detector. The amount of CO_2 is directly proportional to the concentration of carbonaceous material in the sample. Please note this instrument does not incorporate UV digestion.

3.0 Sample Handling and Preservation

3.1 Samples are preserved with H_2SO_4 to pH <2. Samples should be collected without headspace in 40 mL glass vials with Teflon septa tops. Holding time is 28 days from sample collection.

Note: Samples preserved with HCL cannot be analyzed with our instrument.

3.2 Samples for Dissolved Organic Carbon analysis should be filtered and then preserved in the field within 2 hours of collection.

4.0 Reagents

4.1 1000 mg/L "KHP" Stock

2.1248 g Potassium Biphthalate - "KHP" (1-$KOCOC_6H_4$-2-COOH) plus DIH_2O to one liter.

4.2 100 mg/L Working Standard

10 mL 1000 mg/L Stock plus DIH_2O to 100 mL.

4.3 5% Phosphoric Acid

Slowly add 125 mL conc. H_3PO_4 to approximately two liters of DIH_2O. Bring to 2500 uL in the bottle reserved for this reagent.

4.4 Sodium Persulfate

Weigh 20 g $Na_2S_2O_2$ into Teflon bottle reserved for this reagent. Slowly pour boiling DIH_2O into bottle - stop at base of the neck. Swirl gently and wait for bubbles to form (wear heat resistant gloves for this). Squeeze bottle to bring liquid to top of bottle and screw on cap. Shake vigorously. Cool in beaker of cold water. This reagent should be prepared fresh for each analysis.

4.5 Standard Curve - Prepare as follows:

Standard Curve Concentration (mg/L)	**mL 100 mg/L Working Standard**	**mL DI water**
1	1	99
2	2	98
5	5	95
10	10	90
15	15	85
20	20	80

5.0 Procedure

5.1 Use the O.I. Carbon Analyzer for this analysis. Open the touch pad and press "number one" while turning on power (this retains analysis parameters such as sampling time, temperatures etc.). Add fresh 5% H_3PO_4 to the acid bottle and replace the persulfate bottle with one just prepared. Turn on nitrogen gas and adjust to 30 psi.

5.2 Allow instrument to warm up and stabilize baseline. The instrument is on an 8 ½ minute cycle. After an hour or two of repeated DIH_2O blanks, the baseline should be stable. Results in the range of 15-30 volts should be fairly consistent. Only now should the standard curve be run.

5.3 All samples should be checked that pH <2. Record this on the benchsheet.

5.4 Following the Standard Curve, analyze a separate source Laboratory Control Sample (LCS) and an Initial Calibration Blank.

Note: This instrument can have significant carryover following an elevated sample or standard. If there is any question that the sample is "high" (i.e., odor, certain colors or foaming), begin with a ten-fold dilution. If the sample is "low" after all, it can always be rerun undiluted.

5.5 Follow high samples with a blank. This will avoid many potential carryover problems.

5.6 Continuing Calibration Blanks and Verification Standards (CCB's and CCV's) must be run every 10 samples and at the end of the analysis.

5.7 Any sample exceeding the Standard Curve must be diluted and reanalyzed.

5.8 If samples are being filtered by the laboratory for Dissolved Organic Carbon a filtered blank must also be analyzed.

6.0 Calculations

6.1 Analyze the Standard Curve, recording the millivolt responses. Plot mg/L concentration against millivolts. Sample concentrations are read in millivolt. Report results in mg/L.

7.0 Quality Control

7.1 The standard curve consists of a blank, then 1, 2, 5, 10, 15, and 20 mg/L standards. Be sure to record the lot number of the stock standard solution on the benchsheet. The correlation coefficient of the curve must be ≥0.995.

7.2 Calibration verification standards (ICV/CCV's) and calibration blanks (ICB and CCB's) are analyzed every ten samples. ICV and CCV's have a control limit of 90-110% of true value. ICB's and CCB's may not exceed ± 0.5 mg/L.

7.3 One Prep Blank is prepared with each batch of samples of the same matrix. Prep blanks, whether for liquids or solids, must be within the ≤ 0.5 mg/L.

7.4 Any sample which exceeds 10 mg/L must be diluted and reanalyzed.

7.5 A sample duplicate and a matrix spike are performed with every sample batch of up to 20 samples of the same matrix. Duplicate samples must have an RPD ± 20%. Spike recoveries must be 75-125%. Samples failing the matrix spike criteria must have a post-distillation spike performed on it. Matrix spike recovery is calculated with the following equation:

$$MS\ Recovery\ (\%) = \frac{SSR - SR}{SA} * 100$$

where:
SSR = Spike Sample Results
SR = Sample Results
SA = Spike Added (concentration)

The Relative Percent Difference (%RPD) between the sample and duplicate analysis is calculated with the following equation:

$$\%\ RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} * 100$$

where:
RPD = Relative Percent Difference
D_1 = First Sample Value
D_2 = Second Sample Value (duplicate)

7.6 Method Detection Limit Studies (MDL) are determined annually. The MDL is determined by taking 7 samples of known concentration of cyanide and analyzing them. These standards are distilled. The standard deviation is then multiplied by 3.143 to determine the MDL. The resulting MDL must be less then the reporting limit of 0.5 mg/L.

APPENDIX A-16

STANDARD OPERATING PROCEDURE FOR TOTAL ORGANIC CARBON IN SEDIMENT (LLOYD KAHN METHOD)

DETERMINATION OF TOTAL ORGANIC CARBON IN SEDIMENT
Lloyd Kahn Method

Approvals and Signatures

QA Officer: Martha E. Ray Date: 4/17/96

Wet Chemistry Section Head: Daniel G. Meadow Date: 4/17/96

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1.0 Scope and Application

1.1 This method describes protocols for the determination of organic carbon in sediments.

1.2 The detection limit may vary with sample type however the typical reporting limit is 100 mg/Kg as received.

1.3 Data are reported on a mg/Kg dry weight basis and represent the average of at least two results.

2.0 Summary of Method

2.1 Inorganic carbon from carbonates and bicarbonates is removed by treatment with phosphoric acid.

2.2 The organic compounds are decomposed by pyrolysis in the presence of oxygen or air.

2.3 The carbon dioxide that is formed is determined by direct non-dispersive infrared detection, flame ionization gas chromatography after catalytic conversion of the carbon dioxide to methane; thermal conductivity gas chromatography, differential

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thermal conductivity detection by sequential removal of water and carbon dioxide; or thermal conductivity detection following removal of water with magnesium perchlorate.

2.4 Water content is determined on a separate portion of sediment.

3.0 Sample Handling and Preservation

3.1 Collect sediments in glass jars with Teflon or aluminum foil. Cool and maintain at 4 °C. Analyze within 14 days.

4.0 Interferences

4.1 Volatile organics in the sediments may be lost in the decarbonation step resulting in a low bias.

4.2 Bacterial decomposition and volatilization of the organic compounds are minimized by maintaining the sample at 4 °C, analyzing within the specified holding time, and analyzing the wet sample.

5.0 Apparatus

5.1 Drying oven maintained at 103 °to 105 °C.

5.2 Carlo Erba Elemental Analyzer for TOC.

In this apparatus, the sample is pyrolyzed in a inductive type furnace, and the resultant carbon dioxide is chromatographically separated and analyzed by a differential thermal conductivity detector.

5.3 No specific analyzer is recommended as superior. The above listing is for information only and is not intended to restrict the use of other unlisted instruments capable of analyzing TOC. The instruments to be used must have the following specifications:

5.3.1 A combustion boat which is heated in a stream of oxygen or air in a resistance or induction-type furnace to completely convert organic substances to CO_2 and water.

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5.3.2 A means to physically or by measurement technique to separate water and other interferants from CO_2.

5.3.3 A means to quantitatively determine CO_2 with adequate sensitivity (0.01% or 100 mg/kg), and precision (25% at the 95% confidence level as demonstrated by repetitive measurements of a well mixed ocean sediment sample).

5.4 A permanent recording device is present to document the analysis.

6.0 Reagents

6.1 Acetanilide and Sulfanilamide crystals purchased commercially.

6.2 Phosphoric acid solution, 1:19 by volume.

7.0 Procedure

7.1 Thoroughly mix and transfer 10-30 mg to a tared tin capsule.

7.2 Weigh sample to nearest microgram. Record weight in Run Log.

7.3 Place tin capsule/sample into a sample holder (one of two flat bars drilled with 15 numbered wells). Record well number in Run Log.

7.4 Weigh all samples to be prepared, filling both sample holders.

NOTE: **All samples are to be prepared in triplicate. Additionally, a soil LCS must also be prepared in quadruplicate for quality control requirements (See Section 9.3)**

7.5 Add 1-2 drops 1:19 H_3PO_4 and DI water to each capsule. Check for effervescence. Add H_3PO_4 until all signs of effervescence are gone.

NOTE: This procedure will convert inorganic carbonates and bicarbonates to carbon dioxide and eliminate it from the sample.

7.6 Maintain at approximately 75 °C for 1 hour.

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7.7 Crimp top of tin capsule and place into autosampler of Carlo Erba CHNS-O Elemental Analyzer.

7.8 Enter sample ID's and weights in Sample Table Menu. Refer to Carlo Erba SOP for sample table entry and actual analysis.

7.9 Analyze the residue according to the instrument manufacturer's instructions.

7.10 Determine percent residue on a separate sample aliquot.

8.0 Calibration

8.1 Follow Carlo Erba SOP for calibration procedure using sulfanilamide.

9.0 Quality Control

9.1 An ICV/CCV (Acetanilide) must be analyzed every 10 drops and be within 90-110% of the true value.

9.2 An ICB/CCB must be analyzed every 10 drops and be less than the detection limit.

9.3 In January of each year, a well mixed, homogeneous sample is prepared and a series of 15 determinations is analyzed. The standard deviation of this series is determined and posted with the instrument. (See 9.4)

9.4 For each prep batch, a commercially purchased soil LCS must be prepared in quadruplicate. Calculate and highlight the standard deviation.

If the standard deviation for the LCS exceeds the standard deviation limit (as determined in Section 9.3), identify error and rerun all environmental samples in that batch.

9.5 The average of the triplicate results will be reported for each sample unless there is an obvious problem or error associated with a single result. In that event, the average of the remaining two results will be reported. Unless specifically requested, results of a single determination will not be reported.

A Summary page must be presented for each sample indicating the average percent carbon. Convert this result to mg/Kg as received by multiplying by 10,000.

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The Percent Relative Standard Deviation (% R.S.D.) also appears on the summary page, giving a measure of the results' range. The smaller this value, the closer the triplicate results, although it should be remembered that low results, with very little scatter may still yield a high % R.S.D. The % R.S.D. for the LCS is monitored by control chart as an indication "ideal" scatter.

9.6 Samples will be spiked with an NIST certified carbon source. The spike material will be added prior to the removal of the inorganic carbon. All spiked samples must be prepared in duplicate and spike recovery should be 75-125%.

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10.0 Bibliography

Lloyd Kahn, Quality Assurance Specialist, U.S. Environmental Protection Agency, Region II, Determination of Total Organic Carbon in Sediment, July 27, 1988.

APPENDIX A-17

STANDARD OPERATING PROCEDURE FOR PERCENT SOLIDS

Percent Solids
Laboratory Code: IN623

Approvals and Signatures

QA Manager: Kimy B. Watson Date: 7/21/97

Wet Chemistry Manager: D. Meehan Date: 07/21/97

Inorganic Manager: Kristine Aulin Date: 7/21/97

1.0 Scope and Application

1.1 This method describes the procedure for determining the percent solid material in a given solid sample. These results are used predominantly for "solids correction", that is, allowing solid samples to be reported on a dry weight basis.

2.0 Summary of Methods

2.1 Weigh approximately 10 grams of a sample in a pre-weighed dish. Dry the sample at 103-105°C overnight (12-24 hours) but no longer than 24 hours, cool and re-weigh. Percent solid material is then calculated.

3.0 Sample Handling and Preservation

3.1 None

4.0 Procedure

4.1 Record weight of pre-numbered aluminum weighing dish. Weigh and record the weight to the nearest 0.01 g.

4.2 Transfer approximately 5-10 grams of well mixed sample to dish. Make every attempt to distribute sample evenly in dish, and break up large clumps with spatula. Record total weight of dish and sample in grams to the nearest 0.01g.

Note: Some samples may contain standing water. Be sure to mix these samples especially well in order to obtain a truly representative sample.

4.3 Place samples in 103-105°C oven to dry. Record date and time in. Allow samples to dry overnight (12-24 hours) but no longer than 24 hours. If the sample is dried less than 12 hours, it must be documented that constant weight was attained. In the event it is necessary to demonstrate the attainment of constant weight, data must be recorded for a minimum of two repetitive weigh/dry/dessicate/weigh cycles with a minimum of 1 hour drying time in each cycle. Constant weight would be defined as a loss in weight of no greater than 0.01 g between the start weight and final weight of the last cycle.

4.4 When removing samples from oven, check each sample for any signs of incomplete drying. If such signs are found, return to 103-105°C for an additional dry time and record. Record date and time of removal.

4.5 Allow samples to cool for approximately 10 minutes (No need to desiccate, weight will not be effected at this degree of precision.) and reweigh. Again, record weight to the nearest 0.01 gram.

4.6 All bench data is entered in the LMS system (WVAX), where calculations are performed and a batch designation is assigned. Data entry is verified by a second analyst before results are printed.

Calculation:

$$\% \ W/W = \frac{grams_{dry}}{grams_{wet}} * 100$$

$grams_{dry}$ = Weight of dry sample (g) - weight of dish (g)
$grams_{wet}$ = Weight of wet sample (g) - weight of dish (g)

5.0 Quality Control

5.1 One duplicate per sample is analyzed per batch of twenty or fewer samples. Duplicate results are recorded on the results sheet along with the original sample.

5.2 The laboratory LMS system records a % solid determination for the matrix spike sample, however, the % solid determination for a matrix spike sample is not actually performed and the %solid determination recorded in the LMS system is actually that of the parent sample. The recording of the %solid determination for the matrix spike sample is a limitation of the reporting software.

References

1. ILM04.0USEPA CONTRACT LABORATORY PROGRAM, Statement of Work for Inorgranics Analysis, Multi-media Multi-concentration. Publication 9240.1-30

%solid3.wp

APPENDIX A-18

STANDARD OPERATING PROCEDURE FOR ACID DIGESTION OF AQUEOUS SAMPLES FOR TOTAL METALS

Acid Digestion Of Aqueous Samples For Total Metals For Analysis By ICP Spectroscopy Method 3010A:1T

Approvals and Signatures

QA Officer: Martha Roy Date: 10/15/96

Metals Section Head: Kristine L. Aubin Date: 10/15/96

1.0 Scope and Application

1.1 This digestion procedure follows the procedures outlined in SW 846 method 3010A. It is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis, by inductively coupled argon plasma spectroscopy (ICP). The procedure is used to determine total metals.

1.2 Analyze samples prepared by Method 3010A by ICP for the following:

Analyte	CAS #
Aluminum	7429-90-5
Antimony	7440-36-0
Arsenic	7440-38-2
Barium	7440-39-3
Beryllium	7440-41-7
Cadmium	7440-43-9
Calcium	7440-70-2
Chromium	7440-47-3

Analyte	CAS #
Cobalt	7440-48-4
Copper	7440-50-8
Iron	7439-89-6
Lead	7439-92-1
Magnesium	7439-95-4
Manganese	7439-96-5
Molybdenum	7439-98-7
Nickel	7440-02-0
Potassium	7440-09-7
Selenium	7782-49-2
Silver	7440-22-4
Sodium	7440-23-5
Thallium	7440-28-0
Vanadium	7440-62-2
Zinc	7440-66-6

2.0 Summary of Method

2.1 A mixture of nitric acid and the material 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 refluxed with hydrochloric acid and brought up to volume. If sample should go to dryness, it must be discarded and the sample redigested.

3.0 Sample Handling and Preservation

3.1 Samples that cannot be acid preserved at the time of collection because of sampling limitations or transport restrictions, should be acidified with nitric acid to a pH <2 upon receipt in the laboratory.

3.2 The holding time for the preserved sample is 6 months. Analyze samples to meet client turnaround time (typically 30 days).

4.0 Reagents

4.1 1:1 Hydrochloric Acid

Fill container up to the half volume mark with ASTM Type 1 water. Then add concentrated HCl until full. Shake to mix reagent. This is now ready for use.

4.2 Concentrated Nitric Acid

4.3 Matrix Spiking Solution - Prepare according to the following Table.

Compound	Conc (PPM)	Source	mLs Added*	Final Conc (PPM)
Aluminum	10000	Inorganic Ventures	10.0	200
Antimony	1000	Inorganic Ventures	25.0	50
Arsenic	1000	SPEX	2.0	4
Barium	1000	SPEX	100.0	200
Beryllium	1000	Inorganic Ventures	2.5	5
Cadmium	1000	Inorganic Ventures	2.5	5
Chromium	1000	Inorganic Ventures	10.0	20
Cobalt	1000	Inorganic Ventures	25.0	50
Copper	1000	Inorganic Ventures	12.5	25
Iron	10000	Inorganic Ventures	5.0	100
Lead	1000	SPEX	1.0	2

Compound	Conc (PPM)	Source	mLs Added*	Final Conc (PPM)
Manganese	1000	Inorganic Ventures	25.0	50
Nickel	1000	Inorganic Ventures	25.0	50
Selenium	1000	SPEX	0.5	1
Thallium	1000	SPEX	2.5	5
Vanadium	1000	SPEX	25.0	50
Zinc	1000	SPEX	25.0	50

* - Add the above mLs to 25 mLs HCl and 10.0 mLs HNO_3; and then bring to a final volume of 500 mL with ASTM Type 1 water.

Add 1 mLs of this solution to the matrix spike sample plus 0.5 mL of a 10 ppm silver solution into the matrix spike sample.

4.4 Aqueous Laboratory Control Sample (LCS) Solution - A full compound list standard prepared from certified vendor standards. Prepare according to the following table.

Standard ID	Vendor	Amt Used (mL)
AT-2*	Inorganic Ventures	20
1000 ppm Sb	Inorganic Ventures	4
AT-3**	Inorganic Ventures	200
1000 ppm As	Inorganic Ventures	2
1000 ppm Se	Inorganic Ventures	1
1000 ppm Tl	Inorganic Ventures	1
LCSWF***	Inorganic Ventures	10

* - AT-2 is a certified multielement blend which contains 100 ug/mL each: Al, Pb and 50 ug/mL each Ba, Be, B, Cd, Cr, Co, Fe, Mn. Ni, Ag, Sr, V, Zn.

**- AT-3 is a certified multielement blend which contains 500 ug/mL each Al, Ca, Fe, Mg, K, Na.

***- LCSWF is prepared in the following way: Add 2 mL concentrated HNO_3 and 70 mL ASTM Type 1 water into an acid cleaned 100 mL volumetric flask. Add 10 mLs of a certified multielement blend which contains 100 ug/mL As, Tl; 50 ug/mL Cd, Se and 30 ug/mL Pb. Bring to a final volume of 100 mLs with ASTM Type 1 water.

Add 25.0 mL concentrated HCl and 10.0 mL concentrated HNO_3 into an acid cleaned 1 liter volumetric flask with about 200 mL ASTM Type 1 water. Add 20 mLs AT-2 solution and 4 mL Antimony solution, swirl, and add about 200 mL ASTM Type 1 water. Add 200 mL AT-3 solution, swirl, and add about 200 mL ASTM Type 1 water. Add remaining standards in the order they are listed, swirl and bring to a final volume of 1 liter with ASTM Type 1 water. Transfer to a plastic container for storage.

The final concentration of the LCS solution is as follows:

Compound	**Final Stock LCS Concentration (ug/L)**	**Final LCS* Concentration (ug/L) After Digestion**
Aluminum	102000	51000
Antimony	4000	2000
Arsenic	2100	1050
Barium	1000	500
Beryllium	1000	500
Cadmium	1050	525
Calcium	100000	50000
Chromium	1000	500
Cobalt	1000	500
Copper	1000	500
Iron	101000	50500

Compound	Final Stock LCS Concentration (ug/L)	Final LCS* Concentration (ug/L) After Digestion
Lead	2030	1015
Magnesium	100000	50000
Manganese	1000	500
Nickel	1000	500
Potassium	100000	50000
Selenium	1050	525
Silver	1000	500
Sodium	100000	50000
Thallium	1100	550
Vanadium	1000	500
Zinc	1000	500

* - 50 mL of the LCS Stock solution is digested and brought to a final volume of 100 mL.

5.0 Procedure

5.1 Transfer 100 mL of well-mixed sample to a 250 mL acid leached/ASTM Type 1 water rinsed Erlenmeyer flask.

Prepare a preparation blank by taking 100 mL of ASTM Type 1 water.
Prepare the aqueous LCS by taking 50 mL of the LCS Stock Solution.
Prepare separate aliquots of sample for the matrix spike and duplicate samples.

5.2 Add 3 mL of concentrated HNO_3. Cover the flask with a ribbed watch glass and place the flask on a hot plate. Cautiously evaporate to a low volume (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.

5.3 Cool the flask and add another 3 mL portion of concentrated HNO_3. Cover the

beaker with a non-ribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

5.4 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). Again, uncover the flask or (use a ribbed watch glass), and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the flask to go dry.

5.5 Cool the flask and add a small quantity of 1:1 HCl (10 mL/100 mL of final solution) and warm the beaker for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

5.6 Wash down the flask walls and watch glass with ASTM Type 1 water and when necessary, filter or centrifuge the sample to remove silicates and other insoluble material. Adjust the final volume to 100 mL using ASTM Type 1 water and a volumetric flask.

6.0 Quality Assurance

6.1 Digest a preparation blank with every digestion batch. The method blank must not contain any elements with concentrations above the reporting limit, or the associated samples must be re-digested.

6.2 Digest an aqueous Laboratory Control Sample (LCSW) with each digestion batch.

6.3 Digest a matrix spike and replicate sample with each set of 20 samples.

APPENDIX A-19

STANDARD OPERATING PROCEDURE FOR ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS FOR TOTAL METALS

Acid Digestion Of Sediments, Sludges, And Soils
Method 3050A:1T

Approvals and Signatures

QA Officer: Martha Roy Date: 10/15/96

Metals Section Head: Kristine L. Aubin Date: 10/15/96

1.0 Scope and Application

1.1 Method 3050A is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by inductively coupled argon plasma spectroscopy (ICP). This method follows the procedures in SW846 method 3050A. Samples prepared by this method may be analyzed by ICP for all the listed metals:

Analyte	CAS #
Aluminum	7429-90-5
Antimony	7440-36-0
Arsenic	7440-38-2
Barium	7440-39-3
Beryllium	7440-41-7
Cadmium	7440-43-9
Calcium	7440-70-2
Chromium	7440-47-3
Cobalt	7440-48-4
Copper	7440-50-8
Iron	7439-89-6

Analyte	CAS #
Lead	7439-92-1
Magnesium	7439-95-4
Manganese	7439-96-5
Molybdenum	7439-98-7
Nickel	7440-02-0
Osmium	7440-04-2
Potassium	7440-09-7
Selenium	7782-49-2
Silver	7440-22-4
Sodium	7440-23-5
Thallium	7440-28-0
Vanadium	7440-62-2
Zinc	7440-66-6

2.0 Summary of Method

2.1 A representative 1- to 2-g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with hydrochloric acid. The diluted samples have an approximate acid concentration of 5.0% (v/v). A separate sample shall be dried for a total % solids determination.

3.0 Interferences

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste.

4.0 Sample Handling and Preservation

4.1 A minimum sample volume of 100 grams should be collected in non-preserved, plastic or glass pre-cleaned containers.

5.0 Reagents

5.1 1:1 HNO_3

Fill container up to the half volume mark with ASTM Type 1 Water. Then add concentrated HNO_3 until full. Shake to mix reagent. This is now ready for use.

5.2 Concentrated HNO_3

5.3 30 % H_2O_2

5.4 Concentrated HCl

5.5 Laboratory Control Sample Solid (LCSS)- Provided by Certified Independent Source

5.6 Matrix Spiking Solution - Prepare according to the following Table.

Compound	Conc (PPM)	Source	mLs Added*	Final Conc (PPM)
Aluminum	10000	Inorganic Ventures	10.0	200
Antimony	1000	Inorganic Ventures	25.0	50
Arsenic	1000	SPEX	2.0	4
Barium	1000	SPEX	100.0	200
Beryllium	1000	Inorganic Ventures	2.5	5
Cadmium	1000	Inorganic Ventures	2.5	5
Chromium	1000	Inorganic Ventures	10.0	20
Cobalt	1000	Inorganic Ventures	25.0	50
Copper	1000	Inorganic Ventures	12.5	25

Compound	Conc (PPM)	Source	mLs Added*	Final Conc (PPM)
Iron	10000	Inorganic Ventures	5.0	100
Lead	1000	SPEX	1.0	2
Manganese	1000	Inorganic Ventures	25.0	50
Nickel	1000	Inorganic Ventures	25.0	50
Selenium	1000	SPEX	0.5	1
Thallium	1000	SPEX	2.5	5
Vanadium	1000	SPEX	25.0	50
Zinc	1000	SPEX	25.0	50

* - Add the above mLs to 25 mLs HCl and 10.0 mLs HNO_3; and then bring to a final volume of 500 mL with ASTM Type 1 water.

Add 1 mL of this solution plus 0.5 mL of a 10 ppm silver solution into the matrix spike sample.

6.0 Procedure

6.1 Mix the sample thoroughly to achieve homogeneity. Weigh to the nearest 0.01 gram, and transfer to a acid leached/ASTM Type I water rinsed 250 mL Erlenmeyer flask, a 1.00 to 2.00 gram portion of sample.

Prepare a preparation blank that consists of 1.0 to 1.5 grams of ASTM Type 1 water.

Prepare a solid Laboratory Control Sample that consists of 1.0 grams of the Solid LCS material.

Prepare a matrix spike sample and a replicate sample.

6.2 Add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass. Gently reflux the sample at 95°C, for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace watch glass, and reflux for 30 minutes. Repeat this last step to ensure complete oxidation, 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 flask.

6.3 Cool sample and add 2 mL ASTM Type I water and 3 mL of 30% H_2O_2. Cover the beaker with a watch glass and return the covered flask to the hot plate for warming and to start the peroxide reaction.

6.4 Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until general sample appearance is unchanged. Do not add more than a total of 10 mL 30% H_2O_2. Heat until effervescence subsides and cool the flask.

6.5 Add 5 mL of concentrated HCl and 10 mL of ASTM Type I water, return the covered flask to the hot plate, and reflux for additional 15 minutes without boiling. After cooling, dilute to 100 mL with ASTM Type I water. Remove particulates in the digestion that may clog the nebulizer by filtration, centrifugation, allowing the sample to settle.

6.6 Filter through Whatman No. 41 filter paper (or equivalent) and bring to final volume of 100 mL with ASTM Type 1 water.

7.0 Quality Assurance

7.1 Digest a preparation blank with each digestion batch. The method blank must not contain any elements with concentrations above the reporting limit, or the associated samples must be re-digested.

7.2 Digest a solid Laboratory Control Sample (LCSS) with each digestion batch. The LCSS must be within the provided control limits or the associated samples must be re-digested.

7.3 Digest matrix spike and replicate samples with each set of 20 samples of the same matrix.

APPENDIX A-20

STANDARD OPERATING PROCEDURE FOR METALS ANALYSIS BY ICP

Method 6010A
Metals Analysis by
Inductively Coupled Plasma Spectroscopy

Approvals and Signatures

QA Officer: Martha Roy Date: 7/26/96

Metals Section Head: Kristine Aubin Date: 7/26/96

1.0 Scope and Application

1.1 Inductively coupled plasma-atomic emission spectroscopy (ICP) determines trace elements, including metals, in solution. The method is applicable to all of the elements below. All matrices, including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, biota, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

1.2 Elements for which the 6010A method is applicable are listed below. Detection limits will meet those specified in the SW846.

Table 1: Aqueous Reporting Limits (ug/L)

Analyte	CAS #	TJA Trace Simultaneous ICP (ICP4 & ICP 5)	TJA Environ II ICP (ICP3)
Aluminum	7429-90-5	200	200
Antimony	7440-36-0	60	60
Arsenic	7440-38-2	10	100
Barium	7440-39-3	200	200
Beryllium	7440-41-7	5	5

Analyte	CAS #	TJA Trace Simultaneous ICP (ICP4 & ICP 5)	TJA Environ II ICP (ICP3)
Boron	7440-42-8	100	100
Cadmium	7440-43-9	5	5
Calcium	7440-70-2	5000	5000
Chromium	7440-47-3	10	10
Cobalt	7440-48-4	50	50
Copper	7440-50-8	25	25
Iron	7439-89-6	100	100
Lead	7439-92-1	3.0	100
Magnesium	7439-95-4	5000	5000
Manganese	7439-96-5	15	15
Molybdenum	7439-98-7	10	100
Nickel	7440-02-0	40	40
Phosphorus	7723-14-0	250	250
Potassium	7440-09-7	5000	5000
Selenium	7782-49-2	5	100
Silicon	7440-21-3	100	250
Silver	7440-22-4	10	10
Sodium	7440-23-5	5000	5000
Strontium	7440-24-6	10	20
Thallium	7440-28-0	10	100
Tin	7440-31-5	10	100

Analyte	CAS #	TJA Trace Simultaneous ICP (ICP4 & ICP 5)	TJA Environ II ICP (ICP3)
Titanium	7440-32-6	10	20
Vanadium	7440-62-2	50	50
Zinc	7440-66-6	20	20

2.0 Summary of Method

2.0 Digest samples in accordance with the suitable SW846 procedure. Digest water samples in accordance with Inchcape SOP 3010:1T; soil samples in accordance with Inchcape SOP 3050:1T and Biota in accordance with Inchcape SOP 3050MOD.

2.1 This method provides the simultaneous, or sequential, multielemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-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 photo-multiplier-correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

2.2 Each metal is quantified at specific wavelengths of light emitted as the electrons relax to lower energy states. The sample is analyzed by multiple integrations (3 injections for ICP3 and 2 injections for ICP4 and ICP5) and the average integration is converted to a concentration from a calibration curve.

Table 2: Specified Wavelengths (nm)

Analyte	TJA Trace Simultaneous ICP (ICP5)	TJA Trace Simultaneous ICP (ICP4)	TJA Environ II ICP (ICP3)
Aluminum	237.313	308.215	308.215
Antimony	206.838	206.838	206.838
Arsenic	189.042	189.042	193.696
Barium	493.409	493.409	493.409
Beryllium	313.042	313.042	313.042
Boron	-	249.678	249.678
Cadmium	226.501	226.502	228.802
Calcium	317.933	317.933	317.933
Chromium	267.716	267.716	267.716
Cobalt	228.611	228.616	228.616
Copper	324.754	324.754	324.754
Iron	271.441	271.441	259.940
Lead	220.353	220.353	220.353
Magnesium	279.079	279.078	279.079
Manganese	294.920	257.610	257.610
Molybdenum	202.030	202.030	202.030
Nickel	231.601	231.604	231.604
Phosphorus	178.287	-	178.287
Potassium	776.491	766.491	766.491
Selenium	196.026	196.026	196.026

Analyte	TJA Trace Simultaneous ICP (ICP5)	TJA Trace Simultaneous ICP (ICP4)	TJA Environ II ICP (ICP3)
Silicon	-	288.158	288.158
Silver	328.068	328.068	328.068
Sodium	330.232	330.232	588.995
Strontium	421.552	-	407.770
Thallium	190.864	190.864	190.864
Tin	-	189.989	189.990
Titanium	334.941	-	336.121
Vanadium	292.402	292.402	292.402
Zinc	213.851	213.856	213.856

(a) According to the instrument manufacture and laboratory experience, the wavelengths listed are used 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. IDL's, interelement correction factors, and upper ranges must be determined and documented for each wavelength used.

3.0 Interferences

3.1 Since metals emit light at more than one wavelength, the emission peak for a target analyte may be overlapped by that of another metal. The additive effect of this interference causes the target concentration to read artificially high. When common elements such as Al, Fe, or Mg are present in high concentrations, spectral overlap produces an apparent concentration of the interfered target analyte, even in its absence. These apparent or interference concentrations are measured independently, allowing correction of the target analyte concentration. Other spectral interferences can be minimized using background corrections or alternate emission wavelengths for the target analyte.

3.2 Matrix matching and dilution are used to correct for viscosity and surface tension changes between samples.

3.3 Determine interelement correction factors and apply automatically by the instrument.

4.0 Apparatus and Materials

4.1 Three instruments are currently in use:

- Thermo Jarrell-Ash Trace (ICP5) simultaneous inductively coupled plasma emission spectrometer. System includes 150 position autosampler and computer control. (1/96)

- Thermo Jarrell-Ash Trace (ICP4) simultaneous inductively coupled plasma emission spectrometer. System includes 150 position autosampler and computer control. (3/94)

- Thermo Jarrell-Ash Enviro II (ICP3) simultaneous and sequential inductively coupled plasma emission spectrometer. System includes 150 position autosampler and computer control. (1/92)

4.2 Operating conditions - Follow the instructions provided by the instrument manufacturer. Establish sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects for each individual analyte line for the particular instrument. All measurements must be within the instrument linear range where coordination factors are valid. Verify that the instrument configuration and operating conditions satisfy the analytical requirements and maintain quality control data confirming instrument performance and analytical results.

4.3 Class A volumetric flasks

4.4 Class A volumetric pipets

5.0 Digestate Storage and Handling

5.1 Store digestates at room temperature in a secured area.

5.2 Holding times for digestates is 180 days after sample receipt. Analyze samples within the required turnaround time of 30 days from receipt of the SDG.

6.0 Reagents

6.1 ASTM Type 1 water

6.2 All blanks and standards are in a 5% HCl, 2% HNO_3 matrix.

6.3 Argon (minimum purity 99.998%)

6.4 Stock Standard Solutions (for Calibration use) purchased from SPEX certified for high purity.

6.5 Calibration Check Standards (for Initial and Continuing Calibration) purchased from Inorganic Ventures certified for high purity.

6.6 Interference Check Solutions made from standards purchased from SPEX or Inorganic Ventures

7.0 Calibration Preparation

7.1 All calibration standards are prepared from SPEX Plasma Standard stock solutions. See Table 3 at the end of this SOP for the concentrations of calibration standards.

7.2 Intermediate standard solutions are made by quantitively transferring aliquots of concentrated stock standards into a volumetric flask containing ASTM Type 1 water and an aliquot of HNO_3/HCl. When the appropriate metals standards have been added, the solution is brought to volume. The resulting intermediate standard solution is in a 5% HCl, 2% HNO_3 matrix.

7.3 Working standards are made by quantitatively diluting the intermediate standard to the needed concentrations.

7.4 Intermediate and working standards are stored at room temperature in storage bottles. These standards are kept until their expiration date.

8.0 Instrument Calibration

8.1 Each instrument is calibrated according to the manufacturer's recommendations . After the torch is ignited and the instrument's parameters are recorded, the calibration standards are placed in an autosampler. A 5% HCl, 2% HNO_3 matrix solution is used for the calibration blank.

During calibration, multiple integrations (two for the ICP4 and ICP5 and three for ICP3) are performed per standard. There is a 120 second rinse between standards.

8.2 Perform initial calibration daily.

8.3 See Table 4 for typical analysis run sequence.

9.0 Calculations

9.1 The final concentration of an element in the sample is determined in the following way:

Liquids

$$C_{(ug/L)} = \frac{ug}{L_{dig}} * \frac{V_{dig}}{V_{samp}}$$

Where:
ug/L_{dig} = ICP result including all dilution factors
V_{dig} = final digestate volume in mLs
V_{samp} = sample volume in mLs

Solids

$$C_{(mg/Kg)} = \frac{ug}{L_{dig}} * \frac{V_{dig}}{g_{samp}} * \frac{100}{\%\ solids}$$

Where:
ug/L_{dig} = ICP result including all dilution factors
V_{dig} = final distillate volume in Liters
g_{samp} = sample weight in grams

10.0 Quality Control

10.1 Dilute and reanalyze samples that are more concentrated than the determined linear calibration limit.

10.2 Analyze the method blank (prep) per sample batch to determine if contamination or any memory effects are occurring. If the blank is contaminated with any of the elements of interest, and the sample concentration for that element is <10 times the blank; redigest and reanalyze.

10.3 Analyze replicate samples at the frequency of one replicate per batch of 20 samples of the same matrix. Bring the replicate sample through the whole sample preparation and analytical process in duplicate. Use a control limit of +/- 20% RPD for sample values greater than five times the instrument detection limit. If the data are outside this control limit flag the element with a "*" for all the samples of the same matrix associated with that SDG.

10.4 Analyze one matrix spike sample per batch of twenty samples of the same matrix. The matrix spike sample is spiked before the digestion process and treated like any other sample. The control limits for the matrix spike are 75-125%. If any element fails to meet this criteria flag the effected samples with the "N" qualifier. Perform a post digestion spike as described below in the event that the matrix spike analyses is flagged with an N.

10.5 Perform a serial dilution analysis (L)once for each batch of 20 samples of the same matrix. If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit in the original sample), an analysis of a 1:5-dilution should agree within +/- 10% of the original determination. If not, a chemical or physical interference effect should be suspected. Flag all the samples

of the same matrix and concentration within the SDG with an "E" qualifier for that element.

10.6 Analyze a Post Digestate Spike for any element when the pre-digestion spike recovery falls outside the control limits and the sample result does not exceed 4x the spike added (exception Ag). Spike the unspiked aliquot of the sample at 2x the indigenous level or 2x CRDL, whichever is greater. An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. If the spike is not recovered within the specified limits, a matrix effect should be suspected. The spiking solution should be assayed if the problem seems to reoccur on the same element.

10.7 Verify calibration every 10 samples and at the end of the analytical run, using a calibration blank and a check standard. The results of the check standard must agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and reanalyze the previous ten samples.

The results of the calibration blank must be within the control limit of ± the CRDL, if not terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples.

10.8 Verify the interelement and background correction factors at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Do this by analyzing the interference check sample. Results should be within +/- 20% of the true value. If not terminate the analysis, correct the problem, recalibrate, and reanalyze the samples.

10.9 Analyze a CRDL standard at the beginning of each run to verify linearity near the CRDL. Although there are no contract specified control limits on this standard at this time, the laboratory uses ± 25% as a warning there may be a problem.

10.10 Analyze aqueous and solid Laboratory Control Sample for each analyte of interest using the same sample preparations, analytical methods and QA/QC procedures employed for the samples received. Prepare and analyze one aqueous LCS for each group of aqueous sample in the SDG, or for each batch of aqueous samples digested, whichever is more frequent. The control limits for the aqueous LCS are ± 20% (exception Ag and Sb). Prepare and analyze one solid LCS for each group of solid samples in the SDG, or for each batch of solid samples digested, whichever is more frequent. The control limits for the solid LCS are determined

by EPA.

Redigest and reanalyze all associated samples and quality control samples, if the recovery of any element is outside the control limits for the LCS.

10.11 A LRS (Linear Range Standard) is analyzed at the beginning of the run to verify the upper linear range. The highest calibration standard is analyzed for all analytes reported and the found concentration must be within 5% of the true value. If the measurements exceed ± 5%, the instrument is recalibrated for the effected analytes.

Table 3: Calibration Standards (ug/L)

Element	Trace ICP Standards		ICP3 Standards	
Antimony	0	500	0	5000
Aluminum	0	50000	0	50000
Arsenic	0	500	0	5000
Barium	0	1000	0	5000
Beryllium	0	500	0	500
Boron	0	1000	0	1000
Cadmium	0	500	0	500
Calcium	0	50000	0	50000
Chromium	0	1000	0	1000
Cobalt	0	1000	0	1000
Copper	0	1000	0	5000
Iron	0	50000	0	50000
Lead	0	1000	0	5000
Magnesium	0	50000	0	50000
Manganese	0	1000	0	1000
Molybdenum	0	1000	0	5000
Nickel	0	1000	0	1000
Phosphorus	0	1000	0	5000
Potassium	0	50000	0	50000
Selenium	0	500	0	5000
Silicon	0	5000	0	5000
Silver	0	500	0	500

Element	Trace ICP Standards		ICP3 Standards	
Sodium	0	50000	0	50000
Strontium	0	500	0	500
Thallium	0	500	0	5000
Titanium	0	1000	0	1000
Tin	0	1000	0	1000
Vanadium	0	1000	0	5000
Zinc	0	1000	0	5000

Table 4: Typical Analytical Run Sequence For An SDG

Standard 0
Standard 1
LRV
ICV
ICB
CCV
CCB
ICSA
ICSAB
CRI
Preparation Blank
Laboratory Control Sample
5 samples
CCV
CCB
10 samples
CCV
CCB
7 samples (includes MS/DP)
ICSA
ICSAB
CRI
CCV
CCB