METHOD 7580

WHITE PHOSPHORUS (P_4) BY SOLVENT EXTRACTION AND GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 7580 may be used to determine the concentration of white phosphorus (P_4) (CAS Registry No. 7723-14-0) in soil, sediment, and water samples.

1.2 This method includes two different extraction procedures for water samples. The first procedure provides sensitivity on the order of 0.01 µg/L, and may be used to assess compliance with Federal water quality criteria. The second procedure provides sensitivity on the order of 0.1 µg/L. The method includes one procedure for the extraction of soil/sediment samples which provides sensitivity on the order of 1 µg/kg.

1.3 White phosphorus is a toxic, synthetic substance that has been used in poisons, smoke-screens, matches, and fireworks, and has been used as a raw material in the production of phosphoric acid. It has been used in smoke-producing munitions since World War I. White phosphorus is thermodynamically unstable in the presence of atmospheric oxygen. As a result, until recently, the prospect of long-term environmental contamination from smoke munitions was considered unlikely. However, a catastrophic die-off of waterfowl at a US military facility has been traced to the presence of P_4 in salt marsh sediments, and lead to the realization that P_4 can persist in anoxic sedimentary environments.

1.4 While this method is included in Chapter Three, Metallic Analytes, the sample preparation, extraction, and analytical techniques employed are closely related to those described in Chapter Four for organic analytes. Therefore, this method has been written as a stand-alone procedure, describing both the extraction and analytical techniques. Analysts should refer to Method 8000 for additional information on gas chromatographic procedures.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in solvent extraction and gas chromatography. Each analyst must demonstrate the ability to generate acceptable results using this method.

1.6 Because P_4 will spontaneously combust in air, the procedures for the preparation of standards described in Section 5 require the use of a glove box or other suitable enclosed area purged with nitrogen.

2.0 SUMMARY OF METHOD

2.1 Water samples are extracted by one of two procedures, depending on the sensitivity required.

2.1.1 For the more sensitive procedure, a 500 mL water sample is extracted with 50 mL of diethyl ether. The extract is concentrated by back extraction with reagent water, yielding a final extract volume of approximately 1.0 mL. A 1.0 µL aliquot of this extract is injected into a gas chromatograph (GC) equipped with a nitrogen-phosphorus detector (NPD). This procedure provides sensitivity on the order of 0.01 µg/L, and may be used to assess compliance with Federal water quality criteria.

2.1.2 When a less sensitive method is required for water samples, a 30 mL water sample is extracted once with 3.0 mL of isooctane. A 1.0 µL aliquot of the extract is analyzed by GC/NPD. This procedure provides sensitivity on the order of 0.1 µg/L.

2.2 Wet soil or sediment samples are analyzed by extracting a 40 g wet-weight aliquot of the sample with a mixture of 10.0 mL of degassed reagent water and 10.0 mL of isooctane. The extraction is performed in a glass jar on a platform shaker for 18 hours. A 1.0 µL aliquot of the extract is analyzed by GC/NPD. This procedure provides sensitivity on the order of 1 µg/kg.

2.3 The concentration of P_4 in the extract is calculated using peak area (or height) and an external standard calibration procedure. The sample concentration is determined from the extract concentration using the final volume of the sample extract, sample volume (water samples) or sample weight (soils/sediments). Results for soils and sediments are reported on a wet-weight basis.

2.4 Separate calibrations are required for water and soil/sediment samples because the sample extracts are prepared in different solvents (diethyl ether and isooctane).

3.0 INTERFERENCES

To date, no chromatographic interferences with this determination have been reported, in part due to the selectivity of the nitrogen-phosphorus detector. This procedure offers several advantages compared to other procedures described in the literature which determine P_4 by converting it to phosphate, in that background concentrations of phosphate are quite common in many water and sediment samples.

4.0 APPARATUS AND MATERIALS

4.1 500-mL separatory funnels with PTFE stopcocks, for water sample extraction (larger separatory funnels may be employed).

4.2 125-mL separatory funnels with PTFE stopcocks, for back extraction of water samples.

4.3 40-mL amber glass vials (for less sensitive water method).

4.4 120-mL glass vials or jars with PTFE-lined screw caps.

4.5 500-mL graduated cylinder.

4.6 10-mL graduated cylinder.

4.7 4-L (or larger) amber glass bottle with PTFE-lined screw cap (for preparation of the aqueous spiking solution).

4.8 250-mL and 50-mL glass volumetric flasks, with ground-glass stoppers.

4.9 Disposable pasteur pipets.

4.10 Vortex mixer.

4.11 Platform shaker, with table to hold 120-mL vials or jars used for soil extractions.

4.12 Glove box or other suitable system to handle P_4 under a nitrogen atmosphere, complete with purified nitrogen source, gas regulator, and tubing.

4.13 Analytical balance, capable of weighing 0.1 mg.

4.14 Forceps, for handling P_4.

4.15 Gas-tight syringe, 10 µL.

4.16 Razor blades or scalpels, for cutting P_4.

4.17 Gas chromatograph, capable of isothermal operation at 80°C, equipped with a nitrogen-phosphorus detector, data system, and all relevant accessories. Alternate detectors (i.e. FPD (Flame Photometric Detector) equipped with a phosphorus filter) may be used if performance is documented.

4.18 GC column, 15 m wide-bore capillary column, 100% methyl silicone, 3.0 µm film thickness (DB-1, or equivalent).

4.19 Glass vacuum filtration apparatus for degassing reagent water (Supelco 5-8062, or equivalent).

5.0 REAGENTS

Unless otherwise specified, all reagents will be at least ACS reagent grade. All reagents must be checked for purity and contaminants through the analysis of method blanks (see Sec. 8.2).

5.1 White phosphorus, (99% purity), Aldrich Chemical, or equivalent.

5.2 Isooctane (2,2,4-trimethylpentane), ACS spectrophotometric grade.

5.3 Diethyl ether, pesticide grade.

5.4 Reagent Water, Refer to Chapter One for a definition of reagent water. The reagent water must be degassed in a glass vacuum filtration apparatus or other suitable device to remove any traces of oxygen. Oxygen may also be removed from the reagent water by heating the water to 90°C and purging it with clean helium or nitrogen, as is done for reagent water used in the analysis of volatile organics (see Chapter One).

5.5 Nitrogen, prepurified, for glove box.

5.6 Nitrogen, zero grade, for GC carrier gas.

5.7 Hydrogen, zero grade, for NPD detector.

5.8 Preparation of calibration stock standard in toluene: The instrument calibration standards for soil/sediment samples and for water samples extracted with isooctane (Sec. 7.6) are prepared in toluene. A separate set of calibration standards is required for water samples extracted with diethyl ether (see Sec. 5.9).

5.8.1 Cut several pieces of P_4 to the appropriate size under degassed water in a nitrogen atmosphere. Care should be taken to ensure that each piece of freshly cut P_4 is lustrous on all surfaces. Each piece should be dried under a gentle stream of nitrogen.

5.8.2 Place a small freshly cut piece of P_4 (approx. 90 mg) into a preweighed 250-mL volumetric flask containing a small amount of toluene.

5.8.3 Weigh the flask containing the toluene and piece of P_4 to determine the mass of P_4 by difference.

5.8.4 Bring the flask to volume with toluene and shake until the P_4 dissolves. Protect the flask from light by wrapping the flask in aluminum foil.

5.8.5 Calculate the concentration of P_4 in the volumetric flask.

5.8.6 Using the calibration stock standard, prepare 5 calibration standards in isooctane over the linear range of the calibration curve. The lowest concentration standard should be set at or below a sample concentration of 1 µg/kg. For a 40 g (wet weight) sample and a 1 µL injection volume, the concentration of the lowest standard will be approximately 4 µg/L in isooctane. To demonstrate the 0.1 µg/L sensitivity for the water sample procedure in Sec. 7.6, the concentration of the lowest standard must be approximately 1 µg/L in isooctane. The remaining standards should span the linear working range of the chromatographic system (see Method 8000 for a discussion of five-point initial calibration standards).

5.8.7 Store any working stock solutions and calibration standards in the dark at 4°C.

5.9 Preparation of calibration stock standard in diethyl ether. Because of the volatility of diethyl ether, it is likely that calibration standards and stock standards for the water samples extracted by the diethyl ether procedure in Sec. 7.3 will have to be prepared more frequently than those standards in isooctane for the soil/sediment samples procedure.

5.9.1 Using the toluene calibration stock standard prepared in Sections 5.8.1 through 5.8.5, prepare 5 calibration standards in diethyl ether over the linear range of the calibration curve. Since the stock standard is diluted by a factor of approximately 5000, the small amount of toluene is insignificant. The lowest concentration standard should be set at or below a sample concentration of 0.01 µg/L. For a 500-mL water sample, a 1.0 mL final extract volume, and a 1 µL injection volume, the concentration of the standard will be approximately 5 µg/L in diethyl ether. The remaining standards should span the linear working range of the chromatographic system (see Method 8000 for a discussion of five-point initial calibration standards).

5.9.2 Store any working stock solutions and calibration standards in the dark at -20°C.

5.10 Preparation of the aqueous stock solution of P_4 - The solubility of P_4 in water is approximately 3 mg/L. The following instructions involve the preparation of a stock solution from an excess of P_4 (i.e., this should produce a saturated solution of P_4 in water).

5.10.1 Cut a piece of P_4 weighing at least 15 mg, under degassed water in a nitrogen atmosphere such as a glove box. Care should be taken to ensure that the piece of

freshly cut P_4 is lustrous on all surfaces. The piece should be dried under a gentle stream of nitrogen.

5.10.2 Maintaining the nitrogen atmosphere, place the freshly cut piece of P_4 into an amber glass container with a PTFE-lined cap and at least a 4 L capacity.

5.10.3 Fill the container with Type I, degassed reagent grade water, leaving no headspace.

5.10.4 Seal the container, remove it from the nitrogen atmosphere, and constantly agitate the mixture for approximately one week.

5.10.5 As noted above, this procedure involves the use of an excess of P_4. After approximately one week, the concentration of the P_4 in the aqueous stock solution must be determined by extraction with isooctane and analysis using the procedures in Sec. 7.6.

5.11 Preparation of the aqueous spiking solutions - Two different aqueous spiking solutions are required for preparation of matrix spike/matrix spike duplicate aliquots. One solution is used for spiking water samples. The other solution is used for spiking soil/sediment samples.

5.11.1 Based on the concentration of the stock solution determined in Sec. 7.6, prepare an aqueous spiking solution at a concentration of 5 µg/L by diluting the stock solution. A 1.0 mL volume of this spiking solution added to a 500 mL sample will produce a concentration of approximately 0.01 µg/L of P_4.

5.11.2 Based on the concentration of the stock solution determined in Sec. 7.6, prepare a soil spiking solution at a concentration of 40 µg/L by diluting the stock solution. A 1.0 mL volume of this spiking solution added to a 40 g wet soil sample will produce a concentration of approximately 1 µg/kg of P_4.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 White phosphorus is released into the environment from smoke munitions in the form of small, discrete particles. These particles persist in soils, sediments, and may occur as suspended or colloidal particles in anoxic waters. Therefore, some samples or sample aliquots from a given location may contain P_4 particles while others do not. The nature and distribution of P_4 contamination from other, non-military, sources has not been studied, but sample collection procedures should address the likelihood that P_4 is present in discrete particles, and must be designed to ensure that multiple representative samples of the matrix of interest are collected. In addition, soil and sediment samples must be carefully homogenized and subsampled.

6.2 Because P_4 will oxidize on contact with oxygen, care must be taken to limit the contact of the sample with the atmosphere and to minimize any introduction of air into the samples. In addition, work by Walsh and Nadeau (Ref. 1) and others indicate that P_4 may be subject to losses as a result of volatilization from the sample.

6.2.1 Aqueous samples should be poured gently into the sample container to minimize agitation which might drive off the volatile P_4. If bubbling does occur while transferring the sample to the container, the sample should be discarded and another sample collected. Each container should be filled with sample until it overflows. Each container should be tightly sealed with a PTFE-lined cap. The container should then be inverted to check for air bubbles. If any air bubbles are present, a new sample must be collected.

6.2.2 Containers for soil samples should be filled as completely as possible, eliminating as much free air space as practical.

6.3 Samples are preserved by cooling to approximately 4°C. Do NOT adjust the pH of water samples or add chemical preservatives, as these may oxidize the P_4.

6.4 EPA has not established formal holding times for samples containing P_4. However, preliminary data suggest that water samples should be stored at approximately 4°C in the dark, and should be extracted within 5 days of collection. Soil/sediment samples should be stored at approximately 4°C, in the dark, and kept tightly sealed to prevent loss of moisture. When stored in this manner, preliminary data indicate that soil/sediment samples may be held indefinitely.

6.5 Due to the volatility of diethyl ether, water sample extracts prepared with diethyl ether (Sec. 7.3) should be analyzed within 8 hours of extraction, and extracts should be stored in tightly capped containers in a refrigerator until analysis.

6.6 Isooctane extracts of soil/sediment samples (Sec. 7.4) and of water samples (using the less sensitive alternative extraction procedure in Sec. 7.6) should be stored in tightly capped containers in a refrigerator and analyzed within 30 days of extraction.

7.0 PROCEDURE

7.1 Establish the instrument operation conditions, using the information below as guidance.

Column: DB-1, 15 m by 0.53 mm ID with 3.0 µm film thickness
Oven Temp: 80°C (isothermal)
Carrier Gas: Nitrogen
Flow Rate: 30 mL/min

Using these conditions, P_4 will elute between 2.5 and 3.0 minutes, and the entire chromatographic run will typically be less than 5 minutes. Optimize the performance to minimize interferences and maximize sensitivity. Document the operating conditions used.

7.2 Initial calibration

Because of the different solvents used for soil/sediment samples and water samples (by the more sensitive method), separate initial five-point calibrations are required for each solvent. In addition, the nitrogen-phosphorus detector may present problems with long-term stability. Therefore, a 5-point initial calibration must be performed at the beginning of each 12-hour analytical shift during which samples are to be analyzed. The calibration procedures are the same for both solvents, and only the calibration associated with samples to be analyzed that day must be run on that day (i.e., if only water samples will be analyzed, only the calibration standards in diethyl ether need to be analyzed that day).

As a practical matter, if both water and soil/sediment analyses are to be performed, the water sample extracts in diethyl ether should be analyzed first, to avoid evaporation of the solvent. If water samples are extracted using the less sensitive procedure involving isooctane, then both water and soil/sediment extracts may be analyzed using the same initial calibration in isooctane.

Perform either of the initial calibrations each day, using the procedure outlined below. See Method 8000 for further details of external standard calibration procedures.

7.2.1 The instrument is calibrated by injecting 1.0 µL aliquots of each calibration standard. To avoid "memory effects," vary the order of the five standards, or analyze from lowest concentration to highest.

7.2.2 Calculate the calibration factor (CF) for the initial calibration curve as follows:

$$CF = \frac{\text{Area of the peak}}{(\text{Standard concentration in ng/µL})(\text{µL injected})}$$

Peak height may be used for calculating the calibration factor, but may not be as representative to small, broad, or oddly shaped peaks.

7.2.3 The linearity of the calibration is evaluated on the basis of the relative standard deviation of the five calibration factors, in accordance with Method 8000. Calculate the mean CF, the standard deviation (SD) of the CFs, and the relative standard deviation (RSD), as follows.

$$\text{mean CF} = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{n-1}}$$

$$RSD = \frac{SD}{\overline{CF}} \times 100$$

where n is the number of initial calibration standards analyzed.

The calculation of a calibration factor is analogous to the calculation of the slope of a regression line forced through the origin (0,0). Data from the U. S. Army Corps of Engineers indicates that the NPD response is linear over a range of at least 20-fold, and passes through the origin. In order to be used for sample analyses, the RSD of the initial calibration must be less than or equal to 15%. As noted above, the initial calibration must be performed at the beginning of each analytical shift during which samples will be analyzed.

7.3 Water sample extraction - diethyl ether extraction procedure providing sensitivity of approximately 0.01 µg/L. See Sec. 7.6 for the less sensitive isooctane alternative extraction procedure.

7.3.1 Carefully transfer a 500-mL aliquot of the water sample to a 500-mL separatory funnel (a larger separatory funnel may be employed). Add 50 mL of diethyl ether, and shake the separatory funnel for 5 minutes with periodic venting. Allow the sample to stand for 15 minutes, or until phase separation occurs.

Optional Step: Add 16 g of sodium chloride to the mixture of liquids in the separatory funnel to increase and stabilize the ionic strength of the water sample and aid in the phase separation during the extraction. If the sample is seawater, addition of the sodium chloride is not necessary.

7.3.2 Diethyl ether is relatively soluble in water and the solubility is greatly affected by temperature. After phase separation, collect the diethyl ether (usually 3-10 mL) in a 10-mL graduated cylinder, and record the exact volume. Note: The volume of the ether layer will depend on the temperature and the ionic strength of the water sample.

7.3.3 For ease of application in a production laboratory environment, adjust the volume of the diethyl ether extract to a constant volume of 10.0 mL at this point. The extract is then concentrated by back extraction with reagent water in Sec. 7.3.4. The advantage of the use of a constant extract volume here is that it minimizes the need to recalculate the volume of reagent water required for each sample extract, although the latter approach may be employed. See Sec. 7.7 for details of the calculation of the volume of reagent water required.

7.3.4 The volume of the diethyl ether extract is reduced to approximately 1.0 mL by back-extraction with reagent water. Transfer the diethyl ether extract to a 125-mL separatory funnel and add 99.2 mL of reagent water. Shake for 1 minute.

7.3.5 After phase separation, collect the remaining diethyl ether phase in a 10-mL (or smaller) graduated cylinder and record the exact volume. Tightly cap the graduated cylinder until the extract is analyzed. See Sec. 6.4 for a discussion of holding times for these sample extracts.

7.3.6 If no diethyl ether phase separates, check the temperature of the solution. If the temperature is significantly below 25°C, then all of the diethyl ether may remain in solution. There are three practical solutions to this problem.

7.3.6.1 Warm the solution in the separatory funnel to 25°C, and allow the phases to separate.

7.3.6.2 Add small volumes (0.5 mL or less) of fresh diethyl ether to the solution, shake the separatory funnel, and allow the phases to separate. Continue adding fresh ether until the solubility of the ether in the reagent water is exceeded and the extract has been concentrated to approximately 1.0 mL.

7.3.6.3 If this problem persists, calculate the volume of reagent water required at the temperature of the solution (i.e., the ambient laboratory temperature), using Sec. 7.7 and the solubility and density of diethyl ether at the new temperature, and extract another aliquot of the sample and use the newly calculated volume of reagent water for back extraction.

7.3.7 Prepare the water matrix spike/matrix spike duplicate (MS/MSD) aliquots by adding 500 mL of the water sample selected for spiking to each of two 500-mL separatory funnels. Spike each MS/MSD aliquot in the funnel with 1.0 mL of the aqueous spiking solution in Sec. 5.11.1 and swirl gently to mix the contents. Extract and concentrate the MS/MSD aliquots in the same manner as samples, beginning at Sec. 7.3.1.

7.4 Soil/sediment sample extraction

7.4.1 Carefully homogenize the soil/sediment sample in its original container using a spatula. Weigh out 40 g of the homogenized wet sample into a pre-weighed 120-mL glass jar.

7.4.2 Weigh out a separate 5-10 g aliquot of each sample for use in determining the percent moisture. Air-dry each sample in a fume hood for at least a day, then dry this aliquot at 105°C for 24 hours and reweigh. The percent moisture is calculated as:

$$\text{Percent moisture} = \frac{\text{wet weight (g)} - \text{dry weight (g)}}{\text{wet weight (g)}} \times 100$$

As noted in Sec. 2.3, soil/sediment P_4 concentrations are reported on a wet-weight basis using this method. However, the percent moisture is reported separately so that the data user can make comparisons between samples and perform dry weight calculations as necessary.

7.4.3 Add 10.0 mL (9.0 mL for spiked soil samples) of degassed Type I reagent water and 10.0 mL of isooctane the sample in the glass jar from Sec. 7.4.1, and seal the jar with the PTFE-lined cap.

7.4.4 Vortex the jar for 1 minute.

7.4.5 Place the jars on a platform shaker, and shake for 18 hours (or overnight) at 2500 rpm.

7.4.6 After removing the samples from the platform shaker, let the samples stand for about 15 minutes to allow phase separation. If a clear isooctane layer does not form, centrifuge a portion of the sample for 5 min at 2500 rpm.

7.4.7 Using a disposable Pasteur pipet, transfer an aliquot of the isooctane layer to a suitable labeled storage vial with a PTFE-lined cap. See Sec. 6.4 for a discussion of holding times for these sample extracts.

7.4.8 Prepare the MS/MSD aliquots by weighing out two additional 40-g aliquots of the soil/sediment sample chosen for spiking into clean 120-mL glass jars. Add 1.0 mL of the aqueous spiking solution (Sec. 5.11.2) to each jar. Seal each jar immediately, and swirl it until the contents are mixed (approximately five times). Allow the samples to equilibrate for 24 hours before extraction. After 24 hours, extract the samples, beginning at Sec. 7.4.3.

7.5 Sample analysis

7.5.1 Allow the sample extract to warm to room temperature and inject 1.0 µL of the extract (water or soil/sediment) into the GC, using a 10 µL gas tight syringe. Record the retention time and peak area (peak height optional) of P_4 in the sample extract.

7.5.2 Calculate the concentration of P_4 in the water samples as follows:

$$C_s \text{ (ng/L)} = \frac{A_s \times V_f}{\overline{CF} \times V_s \times V_i}$$

where:
A_s = Area of the sample peak
V_f = Final extract volume in L
V_s = Volume of sample extracted in L
V_i = Volume injected in L
and
$\overline{CF}$ = Average calibration factor from the initial calibration in diethyl ether

7.5.3 Calculate the concentration of P_4 in the soil/sediment samples as follows:

$$C_s \text{ (ng/g)} = \frac{A_s \times V_f}{\overline{CF} \times M_s \times V_i}$$

where:
A_s = Area of the sample peak
V_f = Final extract volume in L
M_s = Mass of sample extracted in g
V_i = Volume injected in L
and
$\overline{CF}$ = Average calibration factor from the initial calibration in isooctane

Using the units above, the concentration will be in ng/g, which is equivalent to µg/kg.

For water samples extracted with the isooctane procedure (Sec. 7.6), perform the calculation as described in Sec. 7.6.5.

7.6 Alternative water sample extraction procedure providing sensitivity of approximately 0.1 µg/L. This procedure *must* be used to determine the concentration of the aqueous stock solution in Sec. 5.10.

7.6.1 Add 30 mL of the water sample (or the aqueous stock solution) to a 40-mL vial with a PTFE-lined cap. Add 3.0 mL of isooctane to the vial and cap it tightly.

7.6.2 Shake the vial for 5 minutes, and let stand to allow the phases to separate.

7.6.3 Remove the isooctane layer with a disposable Pasteur pipet.

7.6.4 Analyze a 1.0 µL aliquot of the isooctane using the procedure in Sec. 7.5.1.

7.6.5 Calculate the concentration of P_4 using the equation in Sec. 7.5.3, using 0.0030 L (3.0 mL) as the final extract volume and 0.030 L (30 mL) as the sample volume. Substituting the sample volume for the mass (M_s) in Sec. 7.5.3 will result in a concentration in units of ng/L.

7.7 Calculation of the volume of reagent water needed to concentrate the diethyl ether extract to 1.0 mL.

Diethyl ether is very soluble in water, and given the solubility and the density of diethyl ether, the volume of ether that will dissolve in a known volume of reagent grade water can be calculated. By reversing the calculation, the volume of reagent water that would be necessary to dissolve a specific portion of a diethyl ether extract can be determined. Since the P_4 will remain in the free ether phase, the diethyl ether extract can be safely and effectively be concentrated by back extraction with reagent water.

7.7.1 Both the solubility and density of diethyl ether vary with temperature. At 25°C, the solubility of ether in water is 6.05%, on a weight/weight basis. The density of diethyl ether is 0.7076 g/mL at 25°C. The density of reagent water at 25°C is 0.997 g/mL. Reducing the volume of ether in Sec. 7.3.3, 10 mL, to 1.0 mL will require dissolving 9.0 mL of ether in reagent water.

7.7.2 The volume of "excess" ether is 9.0 mL.

7.7.3 The mass of this ether is (9.0 mL x 0.7076 g/mL) = 6.37 g.

7.7.4 The mass of an aqueous solution saturated with 6.37 g of ether is (6.37 g)/(0.0605) = 105.3 g.

7.7.5 The mass of water in that aqueous solution is (105.3 - 6.37), or 98.9 g.

7.7.6 The volume of water required to dissolve 9.0 mL of ether is (98.9 g)/(0.997 g/mL) = 99.2 mL. Therefore, 99.2 mL of reagent water are added to the diethyl ether extract in Sec. 7.3.4.

7.7.7 Using these relationships, the volume of reagent water needed to concentrate other volumes of diethyl ether can also be calculated. Also, similar calculations can be made for temperatures other than 25°C. For instance, at 20°C, the solubility of diethyl ether in reagent water is 6.89% (w/w), the density of diethyl ether is 0.7133 g/mL, and the density of water is 0.9982 g/mL. Substituting these values into the calculations shown above, the volume of reagent water required to concentrate 10.0 mL of diethyl ether to 1.0 mL at 20°C is 91.7 mL.

7.7.8 Table 1 lists the volumes of reagent water needed to concentrate diethyl ether extracts of various volumes less than 10.0 mL to a final volume of 1.0 mL, for both 20 and 25°C.

7.8 Solid-phase micro-extraction (SPME)

Data from the U. S. Army Corps of Engineers suggest that SPME may be a useful technique for the analysis of P_4. It may be used to screen samples for P_4, by simply exposing the SPME fiber to the water sample, or adding reagent water to a soil/sediment sample and exposing the fiber to the headspace. The fiber is then thermally desorbed in a heated injection port of the GC. Such screening results may be used to differentiate between water samples that require the added sensitivity of the diethyl ether extraction and those that may be adequately treated with the isooctance procedure.

Additionally, SPME may offer an alternative to the use of either solvent in the determination of P_4 in environmental samples. Further work in this area is on-going at the U. S. Army Corps of Engineers, and may be added to later revisions of this method.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control reference sample must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, and with each batch of samples (up to a maximum of 20 environmental samples of a similar matrix), the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control.

8.2.1 Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

8.2.2 The method blank should be carried through all stages of sample preparation and measurement.

8.2.3 For water samples, the method blank consists of a 500 mL volume of reagent water carried through the entire analytical procedure.

8.2.4 For soil/sediment samples, the method blank may be prepared from a 20-g aliquot of a dry soil/sediment sample from an area not contaminated with P_4, or 20-g of clean dry sand. The 20-g aliquot is mixed with 20 mL of reagent water and allowed to stand for one hour.

NOTE: In order to be acceptable, neither the water method blank nor the soil/sediment method blank may contain any P_4 detectable by this method. All samples associated with a contaminated method blank should be re-extracted and reanalyzed.

8.3 Prior to the analysis of any sample extracts, the analyst must perform an initial five-point calibration that meets the performance specifications in Sec. 7.2.3. This initial calibration must be repeated at the beginning of each 12-hour analytical shift during which samples are analyzed. The initial calibration must be performed using the same solvent as the sample extracts to be analyzed, i.e., separate initial calibrations are required for diethyl ether and isooctane.

8.4 The analyst must verify the initial calibration periodically during the course of sample analyses to ensure that the response of the NPD has not drifted. The calibration is verified using the mid-point (i.e., third of five) standard from the initial calibration, as described below.

8.4.1 A total of 10 extracts, including blanks, samples, and MS/MSD aliquots may be analyzed following an initial calibration that meets the specifications in Sec. 7.2.3. After the injection of the tenth extract, the mid-point calibration standard must be injected to verify the calibration.

8.4.2 Based on the response of the calibration verification standard, calculate the calibration factor according to Sec. 7.2.2.

8.4.3 Calculate the percent difference (%D) between the calibration factor calculated from the calibration verification standard (CF_v) and the mean calibration factor from the initial calibration at the beginning of the analytical shift, as follows.

$$\% \text{ Difference} = \frac{\overline{CF} - CF_v}{\overline{CF}} \times 100$$

8.4.4 In order for analysis of samples to continue, the %D must be within ± 15%. Otherwise, analysis must be halted until a new initial calibration is performed.

8.4.5 If the calibration verification meets the ± 15% QC limit, then sample analyses may continue, continuing to use the mean CF from the initial calibration for calculating sample concentrations.

8.4.6 The calibration must be verified after the analysis of each set of 10 extracts of sample, blanks, MS/MSD. The injection of the calibration verification standard itself is not counted as part of the 10 injections. Analyses may continue in this fashion, with calibration verification standards analyzed after each 10 sample extracts, until the end of the 12-hour analytical shift, or until the verification standard fails to meet the ± 15% QC limit.

8.5 Initial demonstration of capability

The ability of the analyst to generate acceptable accuracy and precision using this method is demonstrated through the analysis of spiked aliquots of reagent water, as described below.

8.5.1 Four 500-mL aliquots of reagent water are spiked with the aqueous spiking solution (Sec. 5.11.1) to produce a concentration of approximately 0.01 µg/L of P_4.

8.5.2 The four aliquots are analyzed according to the procedure used for water samples, beginning in Sec. 7.3.

8.5.3 Calculate the recovery of P_4 in each aliquot, using the formula below.

$$\text{Recovery} = \%R = \frac{C_s}{C_n} \times 100$$

where:

C_s = Measured concentration of the spiked sample aliquot

C_n = Nominal (or theoretical) concentration of the spiked sample aliquot

8.5.4 Calculate the mean recovery and the standard deviation of the four recoveries.

8.5.5 The mean recovery must be within the range 30-130%, and the standard deviation of the recoveries must be less than or equal to 30%. These specifications were developed from data provided by the U. S. Army Corps of Engineers, and represent a 95% confidence interval for the recovery of P_4 spiked into four aliquots at approximately 0.01 µg/L (See Table 3). Data from the Corps of Engineers suggest that recoveries in water other than

reagent water (i.e., pond water, tap water, etc.) may be higher than in reagent water, perhaps because of the effects of ionic strength or dissolved constituents on the solubility of P_4.

8.5.6 If the mean recovery or the standard deviation of the recoveries falls outside of these limits, then the analyst must examine the entire analytical process, correct problems or inconsistencies, and repeat this test, beginning at Sec. 8.5.1.

8.6 The laboratory must, on an ongoing basis, prepare and analyze matrix spike and matrix spike duplicate samples to assess the precision and accuracy of the procedure. The MS/MSD aliquots are prepared and analyzed as described in Secs. 7.3.6 and 7.4.8. MS/MSD aliquots should be prepared each batch of samples (up to a maximum of 20 environmental samples of a similar matrix). For laboratories analyzing one to ten samples per month, at least one pair of MS/MSD must be analyzed each month.

The laboratory should develop QC limits for MS/MSD recoveries and precision (RPD), using the procedures in Method 8000. In the absence of laboratory-specific QC limits, the MS/MSD aliquots must have recoveries in the range 75-125% and an RPD less than or equal to 25%.

9.0 METHOD PERFORMANCE

9.1 The Method Detection Limit (MDL) is defined in Sec. 5.0 of Chapter One. MDL values were determined in reagent water, well water, and surface (pond) water, spiked at approximately 0.01 µg/L, and are shown in Table 4. These MDL values were calculated from the results of 10 spiked aliquots of each matrix.

9.2 MDLs were determined for three soil types by spiking the soils with an aqueous solution containing P_4. The MDL values are shown in Table 5, and were determined in clean sand, a sandy loam soil (Lebanon soil), and soil from the Rocky Mountain Arsenal (USAEC Soil). None of these soils were taken from areas where smoke munitions have been employed, and therefore were not expected to contain any P_4. These soil samples were spiked with P_4 at concentrations of approximately 1-2 µg/kg.

9.3 To date, only single laboratory performance data have been generated. Those data indicate that there may be problems with the recovery of P_4 from soils containing high concentrations of metals. Therefore, laboratories employing this method are encouraged to develop in-house performance data including MDLs and accuracy and precision data for routinely encountered matrices. These data should be developed in accordance with the procedures outlined in Method 8000.

10.0 REFERENCES

1. Walsh, M.E. and B. Nadeau, "Preliminary Evaluation of the Analytical Holding Time for White Phosphorus in Surface Water," U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH, CRREL Report 94-13.

2. Taylor, S. and M.E. Walsh, "Optimization of an Analytical Method for Determining White Phosphorus in Contaminated Sediments," U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH, CRREL Report 92-21.

3. Walsh, M. E., and S. Taylor, 1993, "Analytical Method for White Phosphorus in Munitions-Contaminated Sediments," Analytica Chimica Acta, 282: 55-61.

4. Walsh, M.E., 1995, "Analytical Method for White Phosphorus in Water," *Bulletin of Environmental Contamination and Toxicology,* 54(3).

5. Budavari, S., ***et al.***, eds., 1989, The Merck Index, Merck & Co., Rahway, NJ.

TABLE 1
VOLUME OF REAGENT WATER REQUIRED TO CONCENTRATE
DIETHYL ETHER EXTRACTS TO A 1.0 mL FINAL VOLUME AT 20°C AND 25°C

Volume of Diethyl Ether	Volume of Reagent Water Required at 20°C	Volume of Reagent Water Required at 25°C
10.00	91.7	99.2
9.75	89.3	96.4
9.50	86.9	93.7
9.25	84.5	90.9
9.00	82.1	88.2
8.75	79.7	85.4
8.50	77.3	82.7
8.25	74.8	79.9
8.00	72.4	77.1
7.75	70.0	74.4
7.50	67.6	71.6
7.25	65.2	68.9
7.00	62.8	66.1
6.75	60.4	63.4
6.50	57.9	60.6
6.25	55.5	57.9
6.00	53.1	55.1
5.75	50.7	52.4
5.50	48.3	49.6
5.25	45.9	46.8
5.00	43.5	44.1
4.75	41.0	41.3
4.50	38.6	38.6
4.25	36.2	35.8
4.00	33.8	33.1
3.75	31.4	30.3
3.50	29.0	27.6
3.25	26.6	24.8
3.00	24.1	22.0
2.75	21.7	19.3
2.50	19.3	16.5
2.25	16.9	13.8
2.00	14.5	11.0
1.75	12.1	8.3
1.50	9.7	5.5
1.25	7.2	2.8

Solubility of diethyl ether in water is 6.05% (w/w) at 25°C and 6.89% at 20°C.

Density of diethyl ether is 0.7076 g/mL at 25°C and 0.7133 g/mL at 20°C.

Density of water is 0.997 g/mL at 5°C and 0.9982 g/mL at 20°C.

TABLE 2
RECOVERY OF P_4 FROM SPIKED WATER SAMPLES
(ALL VALUES GIVEN AS PERCENT RECOVERY)

	Reagent Water	Well Water	Pond Water
	52	46	92
	77	94	86
	44	87	99
	68	124	82
	69	74	80
	68	91	83
	57	91	84
	64	99	68
	56	91	56
	66	90	68
Mean Recovery	62.1	88.7	79.8
Standard Deviation	9.7	19.6	12.6
Spike Level (µg/L)	0.012	0.0097	0.0101

The concentration results for these replicate samples were used to calculate the MDL values in Table 4.

The two lowest and two highest concentration values from each set of replicates were used to establish the recovery and precision specifications in Sec. 8.5.

TABLE 3
RECOVERY OF P_4 FROM SPIKED SOIL SAMPLES
(ALL VALUES GIVEN AS PERCENT RECOVERY)

	Sand	Lebanon Soil	USAEC Soil
	90	98	76
	90	66	68
	97	86	73
	94	87	74
	96	93	76
	85	82	74
	89	86	74
	94	66	71
	92	102	74
	98	94	70
Mean Recovery	92.5	85.9	73.0
Standard Deviation	4.1	12.4	2.5
Spike Level (µg/kg)	1.99	1.24	0.97

The concentration results for these replicate samples were used to calculate the MDL values in Table 5.

The two lowest and two highest concentration values from each set of replicates were used to establish the recovery and precision specifications in Sec. 8.5.

TABLE 4
METHOD DETECTION LIMITS CALCULATED FOR THREE WATER TYPES

	Reagent Water	Well Water	Pond Water
MDL (µg/L)	0.008	0.009	0.008

These MDLs were calculated from the analyses of 10 replicate aliquots of each water type spiked with P_4 at 0.0097 to 0.012 µg/L. The MDLs were calculated as the Student's *t* value for 10 replicates (2.821) multiplied by the standard deviation of the results for each water type.

TABLE 5
METHOD DETECTION LIMITS CALCULATED FOR THREE SOIL TYPES

	Sand	Lebanon Soil	USAEC Soil
MDL (µg/kg)	0.02	0.43	0.07

These MDLs were calculated from the analyses of 10 replicate aliquots of each soil type spiked with P_4 at 0.97 to 1.99 µg/kg. The MDLs were calculated as the Student's *t* value for 10 replicates (2.821) multiplied by the standard deviation of the results for each soil type.

As can be seen, the MDL values vary significantly. However, if one compares the spiked concentration for each matrix with the MDL value, it is clear that both the Sand and USAEC Soil were not spiked within 3-5 times the estimated detection limit (as required, see Chapter One). The ratio of the spiking level to the MDL for Sand was 9.7, and 14 for the USAEC Soil. In contrast, the ratio for the Lebanon Soil is 2.9. Therefore, the MDL for Lebanon Soil should be considered as more representative of the method performance than either of the other values because it is closer to the 3-5 times the estimated detection limit range.

WHITE PHOSPHORUS (P_4) BY SOLVENT EXTRACTION AND GAS CHROMATOGRAPHY