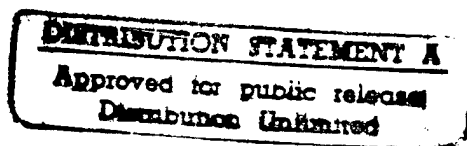


Method for Producing Performance Evaluation Soil/Sediment Samples for White Phosphorus Analysis

Marianne E. Walsh

September 1996



Abstract: The analysis of performance evaluation samples is a routine part of most quality assurance programs. However, performance evaluation samples are not commercially available for many contaminants. This report describes the development of performance evaluation samples for white phosphorus (P₄) analysis. To represent the wide range of concentrations that have been measured in field-contaminated sediment/soil samples, two types of performance evaluation

samples were prepared. High concentration samples contained particulate white phosphorus in wet soil, and concentrations were stable for over 100 days. Low concentration soil samples containing white phosphorus dissolved in water or organic solvent were unstable. When silt-size glass beads were substituted for the soil, and a solution of white phosphorus in mineral oil added, concentrations were stable for over two months.

How to get copies of CRREL technical publications:

Department of Defense personnel and contractors may order reports through the Defense Technical Information Center:

DTIC-BR SUITE 0944
8725 JOHN J KINGMAN RD
FT BELVOIR VA 22060-6218
Telephone 1 800 225 3842
E-mail help@dtic.mil
msorders@dtic.mil
WWW http://www.dtic.dla.mil/

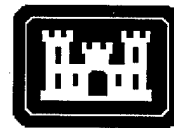
All others may order reports through the National Technical Information Service:

NTIS
5285 PORT ROYAL RD
SPRINGFIELD VA 22161
Telephone 1 703 487 4650
1 703 487 4639 (TDD for the hearing-impaired)
E-mail orders@ntis.fedworld.gov
WWW http://www.fedworld.gov/ntis/ntishome.html

A complete list of all CRREL technical publications is available from:

USACRREL (CECRL-TL)
72 LYME RD
HANOVER NH 03755-1290
Telephone 1 603 646 4338
E-mail techpubs@crrel.usace.army.mil

For information on all aspects of the Cold Regions Research and Engineering Laboratory, visit our World Wide Web site:
<http://www.crrel.usace.army.mil>



**U.S. Army Corps
of Engineers**
Cold Regions Research &
Engineering Laboratory

Method for Producing Performance Evaluation Soil/Sediment Samples for White Phosphorus Analysis

Marianne E. Walsh

September 1996

19961126 032

Prepared for
U.S. ARMY ENVIRONMENTAL CENTER

DTIC QUALITY INSPECTED 4

Approved for public release; distribution is unlimited.

PREFACE

This report was prepared by Marianne E. Walsh, Chemical Engineer, Applied Research Division, Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory. Funding for this work was provided by the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland, Martin H. Stutz, Project Monitor.

The author gratefully acknowledges Dr. Sae-Im Nam and Dr. Thomas F. Jenkins for technical review of the manuscript.

This publication reflects the personal views of the authors and does not suggest or reflect the policy, practices, programs, or doctrine of the U.S. Army or Government of the United States.

The contents of this report are not to be used for advertising or promotional purposes. Citation of brand names does not constitute an official endorsement or approval of the use of such commercial products.

Method for Producing Performance Evaluation Soil/ Sediment Samples for White Phosphorus Analysis

MARIANNE E. WALSH

INTRODUCTION

Site investigations for munitions residues at U.S. Army training areas may include analyses for white phosphorus, which is used by the Army as a smoke producing munition. Although white phosphorus (WP or P_4) is pyrophoric, residues may persist in wet environments (Walsh et al. 1995).

Many laboratories that do not routinely analyze for white phosphorus are now being requested to do so. Unlike other analytes where standard or certified reference materials are available for the preparation of calibration standards and spike solutions, laboratories must prepare standard solutions from commercially available material. Likewise, performance evaluation samples are not available. Therefore laboratories have no way of evaluating their overall analytical recovery.

The objective of this task was to develop and demonstrate a method for producing performance evaluation soil/sediment samples for white phosphorus analysis. These samples may be used as part of a quality assurance program for evaluating the proficiency of a laboratory, verifying an analytical method, comparing analytical methods, or training of new analysts.

APPROACH

We sought to develop performance evaluation samples that are representative of real samples. White phosphorus concentrations vary widely in soil/sediments that were contaminated by detonations of WP munitions. Following the detonation of a white phosphorus-containing projectile, white phosphorus burns, producing a dense white cloud containing phosphoric acid and trace amounts of WP and phosphine (Van Voris et al. 1987). Solid chunks of white phosphorus may be scattered by the detonation (Walsh and Collins 1993), producing white phosphorus concentra-

tions in surface soils/sediments greater than 1,000 $\mu\text{g/g}$ at discrete locations. Between areas of very high concentrations are much larger areas of very low concentrations (0.001 to 0.01 $\mu\text{g/g}$), which are likely produced from deposition of colloidal particles from the cloud and, with time, diffusion from or attenuation of solid chunks of white phosphorus. To mimic the mechanisms by which real samples were contaminated and to be representative of the wide range of concentrations typically found (Table 1), two types of performance evaluation samples were prepared: one at a high concentration containing particulate white phosphorus and one at a low concentration containing dissolved white phosphorus.

METHODS

Preparation of high concentration samples

Production of white phosphorus particles

Particles of WP were produced from molten white phosphorus. Details of the procedure are given in Appendix A; a brief description of the procedure follows. White phosphorus was obtained as sticks (16.1-mm diameter) stored in water from Aldrich Chemical Co. One stick of WP was placed in an 18.3-cm-diam. glass dish under 3 cm of reagent water (MilliQ, Millipore Corporation) and a razor blade was used to obtain a 2-mm slice. The edges of each slice were cut away so that only white phosphorus from the interior of the stick was used. The mass of slice was approximately 700 mg. The piece of WP was transferred under water to a test tube (13 $\times$ 100 mm) and the test tube placed in a 50-mL beaker, which was then placed in a 1-L beaker containing reagent grade water. The 50-mL beaker was used to support the test tube containing WP. Additional test tubes were placed in the 1-L beaker. These test tubes served to isolate the particles of WP, once they were produced.

The water and white phosphorus were heated

Table 1. White phosphorus concentrations found in field samples collected from an Army training area (Racine 1995).

Concentration range ($\mu\text{g/g}$)		Number of samples	Percent of samples
Not detected		1281	66
Detection limit to	0.00099	79	4
0.001 to	0.0099	203	11
0.01 to	0.099	185	10
0.1 to	0.99	72	4
1.0 to	9.99	43	2
10 to	99.99	38	2
100 to	999.9	16	1
1000 to	9,999.9	6	0.3

to 54°C (10°C higher than the melting point of white phosphorus). Then 3- μL droplets (5.46 mg) were obtained from the molten white phosphorus using a Gilson Microman Positive Displacement Pipet (size M25) equipped with disposable capillaries and pistons. Each droplet was transferred under water to an individual test tube. The test tubes containing the white phosphorus droplets were cooled in a refrigerator (4°C). White phosphorus can supercool (i.e., remain liquid below the melting point); thus the water had to be cooled well below 44°C to ensure solidification of the white phosphorus.

Upon solidification, the white phosphorus particles were spherical and translucent with a lustrous surface. Diameters of the particles were measured using a SPI (Swiss Precision Instruments) 6-in. (15.2-cm) caliper with 0.1-mm graduations. Based in the measurement of 127 white phosphorus particles produced in this laboratory by the method described above, the mean ($\pm$ standard deviation) diameter was 1.79 ± 0.06 mm (3.2% relative standard deviation). Based on a density of 1.82 g/cm³, the corresponding mass for a 1.79-mm diameter particle is 5.47 mg, which agrees within 0.01 mg of the mass based on the volume of white phosphorus used to make the particles.

Preparation of soil/sediment samples

Certified reference materials, which are frequently used as performance evaluation samples for most analytes, are thoroughly homogenized and subsamples may be taken for analysis. When the analyte is a heterogeneously distributed particle, like white phosphorus, concentration esti-

mates will vary widely from subsample to subsample depending on the number and size of particles in the subsample. To prevent the introduction of subsampling error for the samples prepared for this project, individual spiked soil samples were prepared such that the whole sample is taken for analysis.

A standard soil was obtained from the U.S. Army Environmental Center (Aberdeen Proving Ground, Maryland). Aliquots (20 g) of soil were weighed into 120-mL jars equipped with Teflon-lined caps. Then sufficient water (10 mL) was added to thoroughly saturate the soil. The jars were capped, sealed with Parafilm, and equilibrated for two weeks in the dark at room temperature.

A single white phosphorus particle was added to each wet soil sample, yielding a white phosphorus concentration of 182 $\mu\text{g/g}$ on a wet soil weight basis [$5460 \mu\text{g} \div (20 \text{ g soil plus } 10 \text{ g water})$]. Samples were tightly sealed with screw caps, sealed with Parafilm and stored at room temperature in the dark. Samples were taken for analysis on days 1, 14, 28, 57, 112, 209 and 288.

Preparation of low concentration samples

Several approaches were tested for the preparation of low concentration samples since lack of stability proved to be a considerable problem.

The procedure that produced samples with relatively stable white phosphorus concentrations was as follows. A stock solution of white phosphorus was prepared by dissolving 90.1 mg of WP in 250 mL of toluene to yield a concentration of 360 mg/L. A spiking solution was made by mixing 1 mL of the stock solution with mineral oil* in a 50.0-mL volumetric flask, and bringing the flask to volume with mineral oil to yield a concentration of 7.2 mg/L. Because of the high viscosity of the mineral oil, care was taken to thoroughly mix this solution by inverting the flask numerous times. Using a positive displacement micropipet, a 25- μL aliquot of the spiking solution was added to a mixture of 30-g glass microbeads (25 μm) (3M Company) wetted with 10 g of water in 120-mL glass jars. (These glass beads are in the size range of silt, which is 3.9 to 62.6 μm .) The mass of white phosphorus added to each 40-g wet sample was 0.18 μg , yielding a white phosphorus concentra-

*Mineral oil (also known as paraffin oil) is a mixture of hydrocarbons from petroleum and may be purchased from several sources (e.g., Aldrich Chemical Co.).

tion in the spiked sample of $0.0045 \mu\text{g/g}$. The jars were capped and stored at room temperature in the dark. Samples were taken from analysis on days 0, 14, 28, and 76.

Procedures that failed to produce stable concentrations in spiked samples include the following (all samples were stored at room temperature in the dark):

1. Repetitive additions of an aqueous solution of white phosphorus to wet soil (AEC Standard) in 120-mL jars.

2. Spiking wet soil (AEC Standard) with an aqueous solution of white phosphorus in ampoules and flame sealing.

3. Incubation of wet soil (AEC Standard) with a large piece (12 g) of solid white phosphorus, removal of the piece of white phosphorus, then dispensing of soil into ampoules and 22-mL vials.

4. Spiking of wet soil (AEC Standard) in ampoules (with and without nitrogen purging) with white phosphorus dissolved in mineral oil.

5. Spiking of wet sand (U.S. Silica) in 22-mL vials with white phosphorus dissolved in mineral oil.

Analysis

Samples were analyzed using SW-846 Method 7580 (U. S. EPA 1995). For this method, water is added to each soil/sediment sample to form a slurry, then the white phosphorus is extracted with isooctane by vigorous shaking. Each sample is shaken in a 120-mL jar. For the performance evalu-

ation samples prepared as described above and stored in 120-mL jars, the analyst added water and solvent directly to the sample. For those samples stored in ampoules, the ampoule was placed into a 120-mL jar containing solvent and water, the jar was capped, and then it was shaken to break the ampoule (Hewitt 1994). For those samples stored in 22-mL vials, the cap was removed from the vial and the vial placed upside-down in a 120-mL jar containing water and solvent.

Samples were shaken for 18 hr, then white phosphorus was determined in the soil extracts using a gas chromatograph equipped with the nitrogen-phosphorus detector. High concentration samples had to be diluted by a factor of 1:10,000 to be within the linear calibration range.

RESULTS AND DISCUSSION

High concentration performance evaluation samples

Wet soils spiked with particles of white phosphorus were stable for greater than 100 days after storage at room temperature in the dark (Fig. 1). After 200 days, some samples appeared to have slightly lower concentrations (Fig. 1). Linear regression of white phosphorus concentration vs. time gives a slope of -0.057 [concentration ($\mu\text{g/g}$)/day] with 95% confidence limits of -0.011 and -0.104 . After 288 days, the loss was only 6%. This apparent loss may be due to a systematic error or

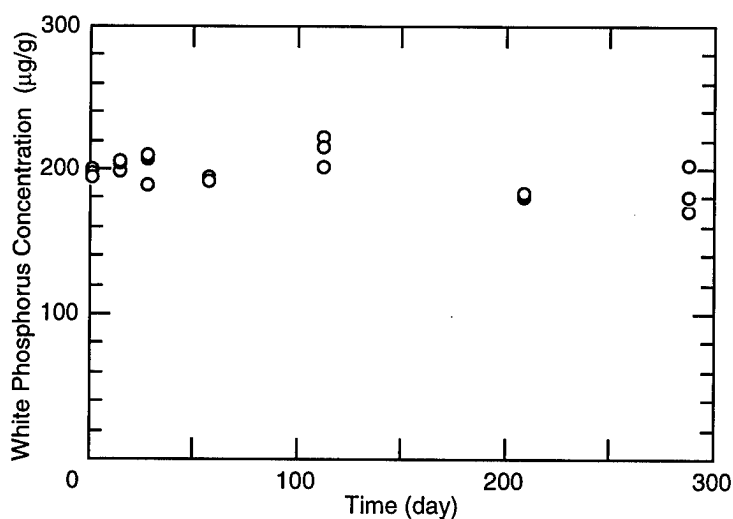


Figure 1. Concentration found in wet soil samples spiked with particulate white phosphorus and stored at room temperature in sealed 120-mL jars.

some loss of white phosphorus.

Systematic error may occur when samples need dilution. We found that the large dilution (by a factor of 10,000) required to analyze these samples introduced some systematic error, the magnitude of which varied with the manner in which the dilutions were performed. The most accurate results were obtained using serial dilution (1 to 100, 1 to 100) using 1.00-mL pipets and 100-mL volumetric flasks. (Calibration standards were also made by serial dilution.) Direct dilutions using microliter syringes were precise, but not accurate, and resulted in an overestimation of concentration. For example, if 1 μ L of solution was measured in a glass microliter syringe and added to 10.0 mL of solvent by simply depressing the plunger of the syringe, the resulting concentration was 108% of the expected concentration. However, if the plunger of the syringe was withdrawn and depressed such that the needle was rinsed into the diluted solution, the resulting concentration was 217% of the expected concentration. This large error shows the importance of proper technique when performing dilutions.

Since serial dilutions require large amounts of solvent, laboratories may choose to do direct dilutions. If so, the magnitude of the systematic error should be evaluated by each laboratory. We performed direct dilutions for all the samples in these experiments, and multiplied the result by a correction factor based on the estimates obtained by a serial dilution of a subset of samples.

At the last sampling time, the white phosphorus particles were isolated for visual examination from the left-over samples. The particle diameters were unchanged, but the surfaces of the particles were not longer translucent. Rather, the surfaces were dull white, indicating that some surface oxidation had occurred. Surface oxidation occurs when solid white phosphorus is stored under water (Nikandrov and Smirnov 1983).

Particles were sliced to examine the interior of the particles. Inside the very thin coating, the particles were translucent, and showed no evidence of change. Loss of WP in only the outer 0.01 mm would be equivalent to the loss of 0.2 mg, which is similar to the magnitude of the loss in some samples. Once formed, a surface oxidation layer should slow any additional changes.

When used for quality assurance, the concentrations of performance evaluation samples should be unknown to the analyst. To vary the concentration of samples spiked with white phosphorus particles, various size particles or multiple par-

ticles could be used rather than the single 5.46-mg particle used in this study.

Low concentration performance evaluation samples

Several methods were tried to produce a sample with a stable low concentration (around 0.001 μ g/g) of white phosphorus. Initially we tried to simulate the mechanism by which soils are contaminated under field conditions, that is, by exposure to water containing dissolved or colloidal white phosphorus. The first method attempted was the spiking of wet soil with an aqueous solution of white phosphorus. This solution was produced by agitating reagent grade water with solid pieces of white phosphorus. The concentration of white phosphorus in the solution was determined by isooctane extraction and gas chromatography to be approximately 0.5 mg/L. Despite a total of three weekly additions of spike solution, for a total of 1.5 μ g of white phosphorus per sample, white phosphorus was not detectable after one week of storage at room temperature in 120-mL jars. Loss of white phosphorus may have been due to volatilization or chemical reaction. To eliminate volatilization, another set of wet soils were spiked and sealed in ampoules with minimal headspace. This method slowed the rate of loss (Table 2a), yet after two weeks of storage the mean concentration of white phosphorus was only 2% of the initial mean concentration.

Next we added a 12-g piece of solid white phosphorus to a kilogram of wet soil and gently agitated the sample for several days. The piece of white phosphorus was removed, and then the wet soil dispensed, either into 22-mL vials (no headspace) or 10-mL flame-sealed ampoules (minimal headspace). This method resulted in white phosphorus soil concentrations much greater than desired, and greater than what would be expected if the water in the samples was saturated with white phosphorus (Table 2b and 2c). These high concentrations indicate that small particles of white phosphorus may have formed due to abrasion from the soil particles during agitation. The heterogeneity between subsamples on day 0 also indicates that small particles of white phosphorus may have been formed. After storage at room temperature, white phosphorus concentrations declined in these samples. Still detectable after over 200 days of storage, the remaining white phosphorus concentration was less than 1% of the mean day 0 concentration (Table 2b and 2c).

After of the first two methods of spiking failed

Table 2. White phosphorus concentrations found after storage at room temperature for samples spiked using a variety of methods.

WP soil concentration (µg/g)				
a. Wet soils spiked with aqueous solution of WP and stored in ampoules.				
	Day 0	Day 7	Day 14	Day 237
	0.0796	0.0289	0.0015	not detected
	0.0901	0.0173	0.0022	not detected
	0.0829	0.0116	0.0013	not detected
Mean=	0.0842	0.0193	0.0017	
Std. Dev. =	0.005	0.009	0.0005	
RSD (%) =	6.4%	46.0%	27.5%	
% of Day 0		23%	2%	
b. Wet soil equilibrated seven days with solid WP then stored in vials.				
	Day 0	Day 14	Day 69	Day 244
	35.1	34.4	17.8	0.004
	39.1	31.4	24.8	0.027
	65.0	34.4	18.4	0.30
Mean=	46.4	33.4	20.3	0.11
Std. Dev. =	16.2	1.7	3.9	0.16
RSD (%) =	35.0%	5.2%	19.0%	149.2%
% of Day 0		72%	44%	0.24%
c. Wet soil equilibrated four days with solid WP then stored in ampoules.				
	Day 0	Day 14	Day 64	Day 239
	6.41	5.69	1.26	0.001
	18.3	2.37	2.13	0.009
	18.7	7.78	0.17	not analyzed
Mean=	14.5	5.3	1.2	0.005
Std. Dev. =	7.0	2.7	1.0	0.006
RSD (%) =	48.3%	51.6%	82.9%	113.1%
% of Day 0		36%	8.20%	0.03%
d. Wet soil spiked with dissolved WP in mineral oil and stored in ampoules.				
	Day 0	Day 14	Day 189	
	0.00796	<0.00044	0.00049	
	0.00849	0.00435	<0.00044	
	0.00772	0.00255	<0.00044	
Mean=	0.0081	0.0024	0.000457	
Std. Dev. =	0.0004	0.0020		
RSD (%) =	4.9%	79.9%		
% of Day 0		30%	6%	

WP soil concentration (µg/g)				
e. Wet soil spiked with dissolved WP in mineral oil and stored nitrogen-purged ampoules.				
	Day 0	Day 14	Day 154	
	0.0095	0.0042	0.0017	
	0.0099	0.0069	0.0021	
	0.0087	0.0040	0.0025	
Mean=	0.0094	0.0050	0.0021	
Std. Dev. =	0.0006	0.0016	0.0004	
RSD (%) =	6.5%	32.2%	19.0%	
% of Day 0		54%	22%	
f. Wet sand and glass microbeads spiked with dissolved WP in mineral oil and stored in 22-mL vials.				
	Day 0	Day 13 Beads	Day 13 Sand	
	0.00397	0.00377	0.00356	
	0.00429	0.00413	0.00362	
	0.00448	0.00448	0.00343	
Mean=	0.00424	0.00413	0.00353	
Std. Dev. =	0.0003	0.0004	0.0001	
RSD (%) =	6.1%	8.6%	2.7%	
% of Day 0		97%	83%	
g. Wet glass microbeads spiked with dissolved WP in mineral oil and stored in 120-mL jars.				
	Day 0	Day 14	Day 28	Day 76
	0.00419	0.00394	0.00364	0.00341
	0.00418	0.00365	0.00262	0.00343
	0.00403	0.00383	0.00378	0.00390
Mean=	0.00413	0.00380	0.00335	0.00358
Std. Dev. =	0.0001	0.0001	0.0006	0.0003
RSD (%) =	2.1%	3.9%	19.0%	7.8%
% of Day 0		92%	81%	87%
Note: Also used aqueous solution and spiked samples in jars, but no WP detected after three additions totaling 1.5 µg				
Ampoules—10 mL, flame-sealed				
Vials—22 mL				
Jars—120 mL				

to produce samples with stable white phosphorus concentrations, we decided to spike wet soils with white phosphorus dissolved in an organic solvent. Solutions of white phosphorus in solvents such as toluene and isooctane are stable for years. We chose mineral oil, a solvent that has high solubility for white phosphorus (12 g/L) (Stich 1953) and has low volatility (for safety during flame-sealing of ampoules). We spiked 19 g of wet soil with 0.18 µg of white phosphorus dissolved in mineral oil (25 µL of a 7.2-mg/L solution), and stored the soils in ampoules with and without nitrogen purging. Again WP concentrations declined with time (Table 2d and 2e).

To isolate what component of the matrix was responsible for the observed losses of white phosphorus, we spiked triplicate samples of dry soil, water, and empty vials with 0.18 µg of white phosphorus dissolved in mineral oil (25 µL of a 7.2-mg/L solution). After two weeks, white phosphorus was not detectable in the dry soil samples. The mean mass ($\pm$ std. dev.) remaining in the water and "empty vial" samples were 0.14 ± 0.05 and 0.18 ± 0.01 µg. Based on these results, something in the soil matrix is responsible for most of the observed losses.

Because white phosphorus can be lost in a variety of chemical reactions (i.e., oxidation by oxygen, halogens, sulfur, acids [e.g., nitric] and most metals, hydrolysis to phosphine) (Mellor 1928, VanWazer 1958), the fate of the WP added to the AEC soil is not known. Unlike the solid piece of white phosphorus used to spike the high concentration samples, where only the surface of the piece was available for reaction, the small amount of dissolved WP added to the samples was totally consumed.

Next we tried spiking matrices that were potentially less reactive than the soil used in previous samples. These matrices were wet sand and glass microbeads. After almost two weeks of storage in 22-mL vials (no headspace), no significant loss was noted for the spiked glass microbeads (Table 2f). While concentrations in the spiked sand were less than day 0, loss was smaller than that observed for the AEC soil.

Finally, we spiked wet glass microbeads stored in 120-mL jars, the same jars used for sample extraction. After 14 days of storage at room temperature, recovery was slightly less than that observed for samples stored in vials without headspace (92% vs. 97%) (Table 2g). White phosphorus concentrations were stable thereafter (up to 76 days) except for one replicate on day 28.

Stability of field-contaminated sediments

Previously, we examined the stability of field-contaminated samples (Table 3). Although sample heterogeneity between subsamples made comparisons difficult, no loss of white phosphorus after 9 to 10 months of storage was apparent in samples representing a wide range of concentrations. The most important factor to maintain sample integrity was to seal the samples tightly to prevent desiccation.

The difference in analyte stability between field-contaminated and laboratory-spiked has been observed previously for other analytes such as TNT (Grant et al. 1995). Similar long-term persistence of pesticides may occur when the compounds are "sequestered in inaccessible microsites within the soil matrix," which reduces bioavailability (Alexander 1995), and are recovered analytically only under vigorous extraction conditions.

Table 3. White phosphorus concentrations found in separate subsamples taken after an extended time interval (Walsh and Taylor 1993).

First analysis concentration (µg/g)	Days between analyses	Second analysis concentration (µg/g)	Number of repeat analyses	Median (µg/g)
0.0036	274	0.0055 to 0.260	8	0.0078
0.011	265	0.011 to 0.550	8	0.014
0.062	267	0.0076 to 0.032	8	0.011
0.150	271	0.070 to 0.520	8	0.097
0.420	313	0.210 to 120	10	0.340

CONCLUSIONS

Performance evaluation samples are an important component of quality assurance/quality control programs. They are especially important for an analytical method that is not performed routinely. This report describes protocols for the preparation of performance evaluation samples containing white phosphorus. Based on previous analyses, white phosphorus concentrations vary widely in samples sent to laboratories for analysis. To represent this wide range of concentrations, two protocols for the preparation of performance evaluation samples were developed, one at a high concentration containing particulate white phosphorus and one at a low concentration containing dissolved white phosphorus.

When particulate white phosphorus was added to wet soils, and the soils were stored in tightly sealed jars, white phosphorus concentrations were stable for over 100 days. Minimal loss of white phosphorus was observed in some samples after 200 days, most likely due to oxidation of the particle surface.

In contrast, loss was significant for white phosphorus dissolved in water or in an organic solvent and spiked onto soil. Stable (over two months) white phosphorus concentrations were achieved only when solutions of white phosphorus in mineral oil were spiked onto an inert matrix, silt-size glass beads. Conversely, long-term monitoring has shown that white phosphorus concentrations are stable in field-contaminated samples if samples are not dried.

LITERATURE CITED

- Alexander, M. (1995) How toxic are toxic chemicals in soil? *Environmental Science and Technology*, **29**(11): 2713-2717.
- Grant, C.L., T.F. Jenkins, K.F. Myers and E.F. McCormick (1995) Holding-time estimates for soils containing explosives residues: Comparison of fortification vs. field contamination. *Environmental Toxicology and Chemistry*, **14**(11): 1865-1874.
- Hewitt, A. (1994) Vapor-fortified QA/QC soil subsamples for the analysis of volatile organic compounds. American Environmental Laboratory, no. 3, p. 1-7.
- Mellor, J.W. (1928) *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*. London: Longmans, Green, and Co.
- Nikandrov, I.S. and S.I. Smirnov (1983) Kinetics of phosphorus oxidation by water. *Zhurnal Prikladnoi Khimii*, **56**(4): 883-885. (Translated by H. Twardowska.)
- Racine, C.H. (1995) Analysis of the Eagle River Flats white phosphorus concentration database. In *Interagency Expanded Site Investigation: Evaluation of White Phosphorus Contamination and Potential Treatability at Eagle River Flats, Alaska* (C.H. Racine and D. Cate, Ed.). USA Cold Regions Research and Engineering Laboratory Contract Report to U.S. Army, Alaska, Directorate of Public Works, FY94 Final Report.
- Stich, C. (1953) Solubility of phosphorus. *Pharmazie*, **8**: 202.
- U.S. EPA (1995) Method 7580: White phosphorus (P₄) by solvent extraction and gas chromatography, In *Test Methods for Evaluating Solid Waste*. U. S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C., SW-846 Update III.
- VanWazer, J.R. (1958) *Phosphorus and Its Compounds*. Vol. I: Chemistry. New York: Interscience Publishers.
- Van Voris, P., M.W. Ligothke, K.M. McFadden, S.W. Li, B.L. Thomas, D.A. Cataldo, T.R. Garland, J.K. Fredrickson, R.M. Bean and D.W. Carlile (1987) Evaluate and characterize mechanisms controlling transport, fate and effects of army smokes in the aerosol wind tunnel: Transport, transformations, fate, and terrestrial ecological effects of red phosphorus-butyl rubber and white phosphorus obscurant smokes. Pacific Northwest Laboratory, Richland, Washington, PNL-6071.
- Walsh, M.E. and C.M. Collins (1993) Distribution of white phosphorus residues from the detonation of 81-mm mortar WP smoke rounds at an upland site. USA Cold Regions Research and Engineering Laboratory, Special Report 93-18.
- Walsh, M.E. and S.T. Taylor (1993) Analytical method for white phosphorus in munitions-contaminated sediments. *Analytica Chimica Acta*, **282**: 55-61.
- Walsh, M.E., C.M. Collins and C.H. Racine (1995) Persistence of white phosphorus particles in sediment. USA Cold Regions Research and Engineering Laboratory, CRREL Report 95-23.

APPENDIX A: DETAILED PROCEDURE FOR PRODUCING WHITE PHOSPHORUS PARTICLES

SCOPE AND APPLICATION

This procedure is for the production of small particles of white phosphorus that may be used to spike soil samples.

SUMMARY OF METHOD

White phosphorus particles are produced by melting white phosphorus in warm water, obtaining microliter droplets of molten white phosphorus, then solidifying the droplets by cooling the water. Particles ranging from 3 to 25 μL (5.5 to 46 mg) may be produced using the equipment included in this procedure.

SAFETY PRECAUTIONS

White phosphorus is pyrophoric, but will not ignite if it is kept under water. It will also not inflame if it is cold ($< 4^{\circ}\text{C}$). For this reason, it should be refrigerated at all times, except during the procedures described below.

White phosphorus is extremely toxic by ingestion (the lowest recorded lethal dose for humans is 1.4 mg/kg of body weight). Fumes may cause chronic poisoning (TLV $0.1 \text{ mg}/\text{m}^3$) so all procedures should be performed in a fume hood. If safety precautions are followed, the procedure described for making white phosphorus particles is not hazardous.

EQUIPMENT AND SUPPLIES

Glassware

Glass dish or tray (Wheaton culture dish no. 350135 (200 $\times$ 80 diameter $\times$ height, mm) or [Pyrex glass drying tray (200 $\times$ 500 $\times$ 50, length $\times$ width $\times$ height, mm)] or equivalent glass container with flat, wide bottom

Test tubes (13 $\times$ 100 mm) (Kimble 13100 or equivalent), one per particle produced plus one

Beakers (50 mL) (Kimble no. 14000-50 or equivalent), two

Beaker, heavy duty (1000 mL) Kimble no. 14005-1000 or equivalent, one

Petri dish, 100 $\times$ 51 mm (Corning 3160-101BO or equivalent)

Utensils

Forceps, preferably Teflon coated (Chemware Norton no. A1069288 or equivalent)

Razor blade, single edged carbon steel (Fisher 12-640 or equivalent)

Tongs, safety, with Teflon-coated tips (Aldrich Z11,543-6 or equivalent)

Thermometer, glass, includes range 20 to 100°C (Fisherbrand 14-997 or equivalent)

Calipers, with 0.1 mm gradations (Swiss Precision Instruments 6-in. caliper or equivalent)

Bottle, wide-mouth, 30 mL, HDPE, (Nalgene 2104-0001 or equivalent), two

Equipment

Hot plate (Corning 6795-500 or equivalent)

Positive displacement micropipet, capacity 3 to 25 μL [Gilson Microman Positive

Displacement Pipet (size M25) or equivalent]

Personal protection equipment

Fume hood
Face shield (Oberon Face-Fit Faceshield no. FF288R or equivalent)
Chemical splash goggles
Apron, Zetex (Fisher No. 17-986-13M or equivalent)
Thermal gloves
Chemical resistant gloves
Bucket of wet sand

Chemicals and Reagents

White phosphorus (P₄) CAS no. 7723-14-0, Aldrich Chemical Co. no. 30,255-4
Water, reagent-grade (Millipore MilliQ or equivalent)

PROCEDURE

Add reagent grade water to the glass dish or tray to a depth of 30 cm. Place dish in fume hood.

Remove the container of white phosphorus from the refrigerator (< 4°C). Place in fume hood and remove the lid from the container (Fig. A1a).

Tilt the container so that the lip is close to the surface of the water in the dish.

Use forceps and gently slide a stick of white phosphorus from the container into the glass dish (Fig. A1b). Since the white phosphorus is cold, it will not ignite from this brief exposure to air. Be certain that there is enough water in the glass dish to completely cover the stick of white phosphorus. The stick of white phosphorus will probably be covered with a white oxidized coating.

Use forceps to hold the white phosphorus steady against the bottom of the dish while slicing through one end of the stick with a razor blade. This cut should leave a lustrous surface.

Cut the stick again to obtain a slice approximately 2 mm thick (Fig. A1c). Then trim the edges of the slice so that all surfaces are lustrous (Fig. A1d).

Place the remaining stick and trimmings in a plastic bottle containing sufficient reagent grade water to cover the white phosphorus. Label the bottle properly, then place the bottle in a refrigerator. Also, label the original container of white phosphorus indicating that some white phosphorus has been removed and return this container to the refrigerator.

Place a test tube horizontally on the bottom of the glass dish. The test tube will fill with water. Use the forceps to place the freshly cut piece of white phosphorus in the test tube (Fig. A1e).

Add approximately 700 mL of reagent grade water to a 1-L beaker, and place the beaker next to the glass dish. Place two 50-mL beakers on the bottom of the 1-L beaker.

Use tongs to transfer the test tube containing the white phosphorus from the glass dish to the 1-L beaker. One of the 50-mL beakers will support the test tube in an upright position (Fig. A1f). Place additional test tubes in the 1-L beaker (Fig. A1g). These test tubes will serve to isolate the white phosphorus particles once they are produced. Be certain that there is sufficient water in the 1-L beaker to completely immerse all test tubes. The top of the water in the beaker should be greater than 5 cm above the tops of the test tubes.

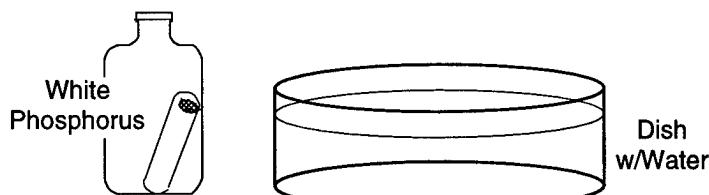
Place the 1-L beaker on a hot plate in the fume hood. Heat until the water reaches 54°C (Fig. A1g). The white phosphorus should melt at 44°C.

Remove the 1-L beaker from the hot plate.

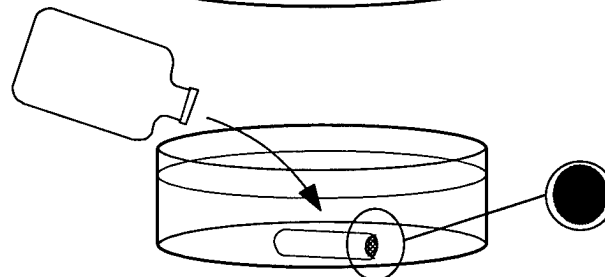
Caution: Molten white phosphorus will ignite if exposed to air. If accidentally exposed to air, immediately cover the fire with water or wet sand.

Depress the plunger and insert the tip of a positive displacement micropipet into the molten white phosphorus. Obtain droplets of the desired size (e.g., 3-μL) from the molten white

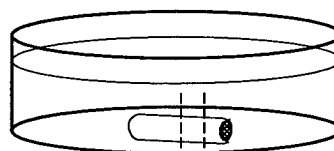
a. Reagent grade water is placed in a glass dish. The water will prevent the WP from igniting.



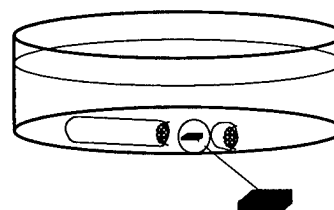
b. The white phosphorus stick must be quickly transferred to the dish.



c. Since the surface of the white phosphorus stick is oxidized, a piece from the interior of the stick must be obtained by slicing through the stick.



d. All freshly cut surfaces should be lustrous.



e. The piece of white phosphorus is transferred to a small test tube.

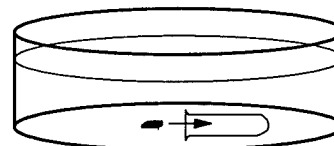
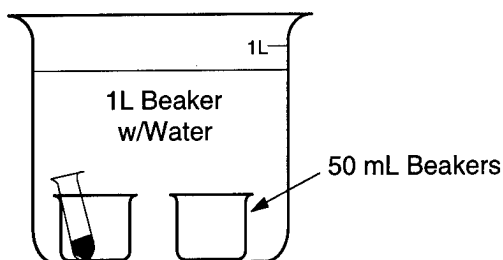


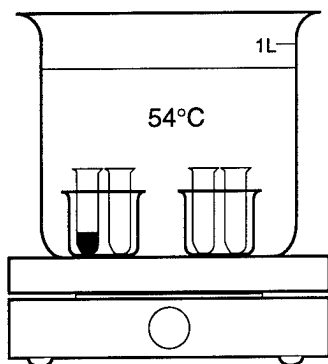
Figure A1. Procedure for producing white phosphorus particles.

phosphorus by slowly releasing the plunger of the positive displacement micropipet (Fig. A1h). Being certain to keep the tip of the micropipet **underwater**, transfer each droplet to an individual test tube (two droplets must not be placed in an individual test tube since the molten white phosphorus droplets will merge to form a larger droplet) (Fig. A1h). Test tubes may be removed from the beaker as needed, and replaced with new test tubes. To maintain the water level, test tubes should be filled with water prior to placement in the 1-L beaker. If several particles are made, the water may need to be reheated by returning the 1-L beaker to the hot plate. Be certain to remove the 1-L beaker from the hot plate prior to making more droplets.

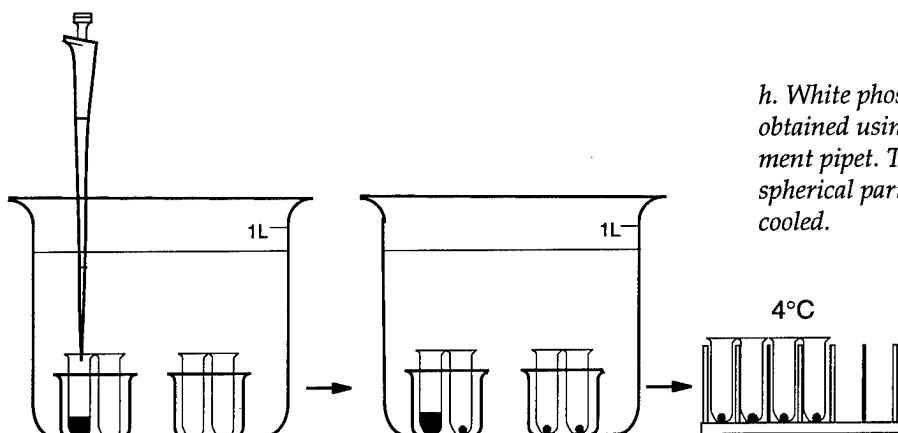
To solidify the droplets of white phosphorus, place the test tubes containing the droplets of white phosphorus in a refrigerator at 4°C (Fig. A1h). White phosphorus can supercool (i.e.,



f. The test tube containing the white phosphorus is placed in a large beaker containing water.



g. The water in the beaker is heated above the melting point of white phosphorus.



h. White phosphorus droplets are obtained using a positive displacement pipet. The droplets will form spherical particles once they are cooled.

Figure A1 (cont'd). Procedure for producing white phosphorus particles.

remain liquid below the melting point); thus the water should be cooled well below 44°C to ensure solidification of the white phosphorus.

Upon solidification, the 3- μ L droplets will maintain a spherical shape; larger droplets will be ovoid. The particle dimensions may be measured by transferring the particles to a petri dish containing reagent grade water and measuring with a calipers. Particles should be colorless and translucent with a lustrous surface. If the particles are exposed to bright light, they will turn yellow due to the formation of red phosphorus; therefore the particles should be shielded from direct light while they are measured.

Once measured, particles should be transferred quickly to a bottle containing reagent grade water and chilled to 4°C in the dark.

Particles may be stored at 4°C for approximately 48 hr. With time, a dull, white film will form on the outer surface of each particle due to oxidation by dissolved oxygen in the water.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestion for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE

September 1996

3. REPORT TYPE AND DATES COVERED

4. TITLE AND SUBTITLE

Method for Producing Performance Evaluation
Soil/Sediment Samples for White Phosphorus Analysis

5. FUNDING NUMBERS

6. AUTHORS

Marianne E. Walsh

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Cold Regions Research and Engineering Laboratory
72 Lyme Road
Hanover, N.H. 03755-1290

8. PERFORMING ORGANIZATION
REPORT NUMBER

Special Report 96-18

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Environmental Center
Aberdeen Proving Ground, Maryland 21010-5401

10. SPONSORING/MONITORING
AGENCY REPORT NUMBER

SFIM-AEC-ET-CR-96159

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.
Available from NTIS, Springfield, Virginia 22161

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The analysis of performance evaluation samples is a routine part of most quality assurance programs. However, performance evaluation samples are not commercially available for many contaminants. This report describes the development of performance evaluation samples for white phosphorus (P_4) analysis. To represent the wide range of concentrations that have been measured in field-contaminated sediment/soil samples, two types of performance evaluation samples were prepared. High concentration samples contained particulate white phosphorus in wet soil, and concentrations were stable for over 100 days. Low concentration soil samples containing white phosphorus dissolved in water or organic solvent were unstable. When silt-size glass beads were substituted for the soil, and a solution of white phosphorus in mineral oil added, concentrations were stable for over two months.

14. SUBJECT TERMS

Calibration standards
Evaluation samples
Stability

Storage losses
White phosphorus

15. NUMBER OF PAGES
16

16. PRICE CODE

17. SECURITY CLASSIFICATION
OF REPORT

UNCLASSIFIED

18. SECURITY CLASSIFICATION
OF THIS PAGE

UNCLASSIFIED

19. SECURITY CLASSIFICATION
OF ABSTRACT

UNCLASSIFIED

20. LIMITATION OF ABSTRACT

UL