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Analytical Method for White Phosphorus in Water

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White phosphorus (P_4) is a toxic, synthetic substance that has been used in poisons, smoke-screens, matches, and fireworks and as a raw material to produce phosphoric acid (Parkes 1951). Environmental contamination with P_4 has occurred at facilities that either produce or use P_4 (Jangaard 1972, Pearson et al. 1976) and areas where P_4 munitions have been used (Racine et al. 1992, Racine et al. 1993). While thermodynamically unstable in aqueous solutions (Pourbaix 1966), P_4 residues persist in aquatic environments and have caused massive mortality of fish (Jangaard 1972) and waterfowl (Racine et al. 1992).

Various water quality criteria for the protection of aquatic organisms have been calculated; they range from 0.01 (Davidson et al. 1987) to 0.04 µg/L (Bentley et al. 1978). For the protection of human health, the Environmental Protection Agency has issued a lifetime health advisory (HA) of 0.1 µg/L; because of the extreme toxicity of P_4 following ingestion, HAs for one-day, ten-day, and longer-term exposures are not recommended (Gordon et al. 1990).

P_4-contaminated water may contain suspended (colloidal) and dissolved P_4 (Dacre and Rosenblatt 1974). Larger particles (200 - 400 µm) may also be suspended (Peer 1972). While the aqueous solubility of P_4 is approximately 3 mg/L (Stich 1953), aqueous suspensions containing 200 mg/L may be produced by dispersion of molten P_4 (Bullock and Newlands 1969).

A specific analytical method for the determination of P_4 in water was developed in conjunction with studies of the severe adverse environmental impact of a release of effluent from a P_4 production facility in Newfoundland, Canada (Addison and Ackman 1970). This method involved the extraction of P_4 from water by a few minutes of vigorous shaking with an organic solvent, either benzene or isooctane. The ratio of water to solvent was 2:1 v/v. P_4 in the extract was then determined by packed-column gas chromatography with a flame photometric detector. The minimum detectable concentration for this method was estimated to be 0.1 µg/L using a 5-µL injection with a precision of ±100% at this concentration. Concentration of the extract by blowdown under an inert gas increased the sensitivity of the method, but further reduced analytical precision.

Environmental assessments at Pine Bluff Arsenal, Arkansas, USA, the site where P_4 munitions are produced, required an analytical method capable of detecting 0.01 µg/L. Lai and Rosenblatt (1977) developed a method sensitive enough to meet this criterion that was based on solvent extraction with benzene followed by neutron activation analysis. The authors reported poor extraction efficiency if the ratio of water to benzene was greater than 10:1. Concentration of the extract by solvent evaporation under an argon atmosphere at room temperature was unsuccessful since P_4 was lost with the solvent, presumably by volatilization.

While the neutron activation method proved to be sufficiently sensitive, the required instrumentation is not available in most analytical laboratories. The objective of this work was to develop an analytical method capable of meeting water quality criteria for the protection of aquatic organisms that uses standard analytical instrumentation. The development focused on a preconcentration step suitable for a volatile, air-sensitive chemical. A nonevaporative preconcentration step, similar to that reported by Jenkins and Miyares (1991), is used that takes advantage of the favorable partitioning of P_4 between organic and aqueous phases (K_{OW} = 1200 [Spanggord et al. 1985]) and the relatively high solubility of diethyl ether in water (6.9% w/w at 20°C). P_4 is extracted from water using diethyl ether (10:1 water:solvent ratio). The ether phase is collected, then reduced in volume by shaking with reagent-grade water. By using the appropriate volume of water, excess ether is dissolved away, resulting in a preconcentration factor of 1000 while heat is avoided and loss of P_4 by volatilization minimized. P_4 is then determined by capillary gas chromatography and a nitrogen-phosphorus detector.

MATERIALS AND METHODS

An analytical standard for P_4 was obtained from Aldrich Chemical Co. (Milwaukee, WI). The P_4 was supplied as a 5-g stick with a white coating under water. Pieces (100 - 300 mg) from the stick were obtained by placing the stick in degassed water in a nitrogen-purged glove bag and cutting with a razor blade. Care was taken to ensure that the surfaces of each piece of P_4 were freshly cut, lustrous in appearance, and showed no evidence of a white coating. These pieces were used to prepare solutions as described below.

A stock solution for calibration standards was prepared under nitrogen by dissolving 250 mg of P_4 in 0.50 L isooctane (Aldrich Chemical Co.). Standards over the range 3.5 to 70 µg/L were prepared by diluting of the stock solution with isooctane or diethyl ether. Standards in isooctane are stable for months stored in ground glass stoppered flasks in the dark at 4°C. Standards in ether were prepared the same day of analysis.

Aqueous solutions of P_4 were prepared by placing pieces of P_4 into an amber jug containing 4 L of Type I water (MilliQ, Millipore) with no headspace and agitating the jug for over 60 days.

Field samples were obtained from Eagle River Flats, Fort Richardson, Alaska, in amber glass bottles filled so that there was no headspace. Samples were maintained at 4°C until extracted. Samples were extracted and analyzed within 5 days of collection.

Two methods were used to extract water samples. The first method was based on previous work (Addison and Ackman 1970). A 30-mL subsample was shaken for 5 min with 3.00 mL isooctane in a 40-mL amber vial. Then the isooctane layer was taken for analysis. For the second method, a 500-mL aliquot of water was extracted with 50 mL of diethyl ether by shaking in a 500-mL separatory funnel for 5 min. After phase separation, all of the ether layer was collected. The volume of the ether layer recovered varied depending on the temperature and the ionic strength of the samples; it generally ranged from 3 to 10 mL. The volume of the ether layer was further reduced to approximately 0.5 mL by adding the ether extract to approximately 50 mL of reagent-grade water in a 125-mL separatory funnel and shaking for 1 min. After phase separation, the ether layer was collected in a 10-mL graduated cylinder and the exact volume measured. P_4 concentration in the extract was then determined by gas chromatography. Extracts were analyzed immediately to minimize loss due to solvent evaporation.

P_4 was determined by injecting a 1.0-µL aliquot of the isooctane or ether extract on-column into an SRI Model 8610 gas chromatograph equipped with a nitrogen-phosphorus detector. The methylsilicone fused silica column (J and W DB-1, 0.53-mm-I.D., 15-m, 3.0-µm film thickness) was maintained at 80°C. The carrier gas was nitrogen set at 30 mL/min. Under these conditions, P_4 eluted at 2 min.

RESULTS AND DISCUSSION

An initial test of this procedure was conducted using an aqueous test solution prepared by sequential dilution of the aqueous P_4 stock. The objective was to determine if sufficient preconcentration could be obtained by extraction of P_4 from 500 mL of water with 50 mL of ether, followed by nonevaporative reduction of the volume of the ether extract to 0.5 mL by dissolution in reagent-grade water. The concentration of the aqueous stock solution, as determined by isooctane extraction followed by gas chromatography, was 650 μg/L. An aqueous test solution was prepared by sequential dilution of the stock so that the estimated concentration of the test solution was 0.016 μg/L. Three 500-mL aliquots were processed according to the method outlined above. The P_4 concentrations found were 0.007 μg/L, 0.016 μg/L, and 0.019 μg/L. Total processing time, including extraction and analysis, was about 30 min per sample. Based on these results, this technique appeared to provide sufficient minimum detectability to meet water quality criteria, and further tests were performed to determine the method detection limit, recovery, and performance with field samples.

A method detection limit (MDL) was determined by extracting seven replicate 500-mL water samples with P_4 concentration in the range of 0.01 μg/L (Federal Register 1984). To prepare a bulk aqueous sample, approximately 3 mL of the P_4 aqueous stock solution was added to a 1-L amber bottle containing reagent-grade water. The bottle was filled with reagent-grade water, then inverted several times over a 10-min period. An aliquot was taken, extracted with isooctane, and the P_4 was determined. The concentration of P_4 was 2 μg/L. A further 1:100 dilution was made by transferring 40 mL of the 2 μg/L aqueous solution into a 4-L amber glass jug containing reagent-grade water, then filling the jug with reagent-grade water. This bulk aqueous sample was mixed by inverting the jug for 10 min, then seven 500-mL aliquots were extracted with 50 mL of diethyl ether. The volume of ether recovered ranged from 3 to 4 mL. This volume was reduced to approximately 0.5 mL by mixing it with 20 - 30 mL of reagent grade water in a 125-mL separatory funnel. The actual volume recovered was measured in a 10-mL graduated cylinder and was used to calculate the concentration.

P_4 was easily detectable in each of the seven samples; concentrations found ranged from 0.022 to 0.031 μg/L (Table 1). An MDL of 0.011 μg/L was obtained.

To estimate recovery, seven water samples (500 mL) were fortified with 0.5 mL of a P_4 spike solution prepared in ether to yield an aqueous P_4 concentration of 0.07 μg/L. Mean recovery was $107\pm12\%$.

To test how the method would perform with actual samples, twenty-one 1-L water samples were collected from a field site contaminated with residues from P_4 munitions (Racine et al. 1993). A sediment sample was also collected at each location. The sediment samples were analyzed for

Table 1. P_4 concentrations found following extraction with diethyl ether in seven replicate 500-mL aliquots of a bulk spiked aqueous sample.

Aliquot (500 mL)	P_4 Conc. (µg/L)
1	0.027
2	0.029
3	0.022
4	0.030
5	0.023
6	0.031
7	0.030
mean=	0.027
std. dev.=	0.0036
$t_{(n-1, \alpha=0.99)}$=	3.143
MDL=	0.011

P_4 using the gas chromatographic procedure described by Walsh and Taylor (1993). For each water sample, two subsamples were extracted, one using the isooctane extraction procedure of Addison and Ackman (1970) and one using the diethyl ether procedure described above. Of these 21 samples, P_4 was not detectable using the isooctane extraction where the preconcentration factor is ten. However, P_4 was detectable in six samples using the ether extraction procedure where the preconcentration factor is 1000. Aqueous concentrations ranged from 0.011 to 0.069 µg/L. These six positive water samples were collected from the same locations as the only six sediment samples where P_4 was detected. However, the concentrations of P_4 found in the water were not correlated with the concentrations found in the sediment (Table 2). All locations were in open water ponded areas where significant dilution with uncontaminated water is possible.

Table 2. P_4 concentrations found in water and sediment samples collected from a field site contaminated with residues of P_4 munitions.

Sample	P_4 Conc. in Water (µg/L)	P_4 Conc. in Sediment (µg/g)
1	0.011	0.079
2	0.013	0.43
3	0.016	1.6
4	0.020	1700
5	0.043	0.0143
6	0.069	0.205

The volume of ether recovered varied with the conductivity and temperature of the sample. Based on the solubility of ether in water

(6.89% w/w at 20°C and 6.05% at 25°C) and the density of ether (0.7133 g/mL at 20°C and 0.7076 g/mL at 25°C), the volume of ether recoverable when 50 mL of ether are mixed with 500 mL of pure water with temperatures between 22 and 25°C will range from 1 to 5 mL (Windholz, et al. 1976). As the aqueous concentration of electrolytes increases, the volume of recoverable ether will increase due to salting-out of the organic phase (James 1986). The conductivity of the field samples ranged from 0.07 to 51 mmhos/cm with a mean of 18.2±17.4 mmhos/cm. The volume of ether recovered ranged from 0.4 to 17 mL with a mean of 6.7±5.0 mL. The lowest volume recovered corresponded to a sample that had not warmed to room temperature prior to extraction; the conductivity of the sample was 3.9 mmhos/cm. Volumes greater than 10 mL were recovered from samples with conductivities exceeding 30 mmhos/cm. In all cases, the volume was easily reduced to approximately 0.5 mL by mixing the recovered ether with reagent-grade water, the volume of which was adjusted according to the volume of ether added. An example calculation is as follows for the case where 5.0 mL of ether is recovered from a sample at 25°C:

1. Volume of excess ether = 5.0 mL - 0.5 mL = 4.5 mL
2. Mass of excess ether = 4.5 mL X 0.7076 g/mL = 3.18 g
3. Mass of aqueous solution saturated with 3.18 g ether = 3.18 g/0.0605 = 52.6 g
4. Mass of water in aqueous solution saturated with 3.18 g ether = 52.6 g - 3.18 g = 49.4 g
5. Volume of water required to dissolve 4.5 mL ether at 25°C = 49.4 g/0.997 g/ml = 49.5 mL

Calculations need only be made once, if the results are entered into a table for future reference.

Further work is being performed to evaluate the pre-extraction holding times for P_4 in aqueous samples. Further work is also required to determine if filtration may be used to differentiate suspended from dissolved P_4. In the mean time, the procedure as outlined here provides a technique to measure P_4 at the current water quality criteria. The nonevaporative/preconcentration method described here may be suitable for other volatile or thermally degradable non-polar chemicals since it does not rely on solvent evaporation.

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