Phosphorus Pentachloride

Analyte:	Phosphate	Method No.:	S257
Matrix:	Air	Range:	0.55-2.00 mg/cu m
OSHA Standard:	1.0 mg/cu m	Precision ($\overline{CV}_T$):	0.053
Procedure	Filter/bubbler collection in water, complexation, colorimetric measurement	Validation Date:	5/12/78

1. Synopsis

1.1 A known volume of air is drawn through a PVC filter followed by a midget bubbler containing 15 mL of distilled water to trap the phosphorus pentachloride present.

The contents of the bubbler are reacted with sodium molybdate and hydrazine sulfate to form the heteropoly blue complex.

The absorbance of the resulting solution is determined at 830 nm and is used as a measure of the amount of phosphorus present; the equivalent amount of phosphorus pentachloride is calculated.

2. Working Range, Sensitivity and Detection Limit

This method was validated over the range 0.553-2.001 mg/cu m using a 48-liter sample.

A concentration of 0.42 mg/cu m of phosphorus pentachloride can be determined in a 48-liter air sample based on a difference of 0.05 absorbance unit from the blank using a 1-cm cell.

3. Interferences

Particulate phosphate is removed by using a 2.0 µm PVC filter connected in front of the midget bubbler.

3.2 Any compound containing phosphorus in the +5 oxidation state and which exists in the atmosphere as a water-soluble vapor could interfere with this determination.

4. Precision and Accuracy

The coefficient of variation ($\overline{CV}_T$) for the total sampling and analytical method over the range of 0.553-2.001 mg/cu m is 0.0528. This value corresponds to a 0.05 mg/cu m standard deviation at the OSHA standard level. Statistical informa-

tion and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

In validation experiments, this method was found to be capable of coming within ±25% of the "true value" on the average of 95% of the time over the validation range. The concentrations obtained at 0.5, 1, and 2 times the OSHA enviornmental limit were 5.0% lower than the dynamically generated test concentrations (n=18). The analytical method recovery was determined to be 0.951 for a collector loading of 53.7 µg. In storage stability studies, the mean of samples analyzed after seven days was within 4.6% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

5.1 Collected samples are analyzed by means of a quick and simple method.

A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.

The bubblers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the bubblers during shipping.

The precision of the method may be limited by the reproducibility of the pressure drop across the prefilter and bubbler This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter/bubbler combination only.

6. Apparatus

Sampling Equipment. The sampling unit for the collection of personal samples for the determination of phosphorus pentachloride consists of the following components:

6.1.1 Prefilter Unit. The prefilter unit, which is used to remove particulate interferences, consists of a 37-mm diameter polyvinyl chloride membrane filter with a pore size of 2.0 micrometer contained in a 37-mm two-piece filter holder. The filter is supported by a 37-mm stainless steel screen (Mine Safety Appliances Co. Cat. No. 456224 or equivalent).

6.1.2 A glass midget bubbler containing distilled water.

6.1.3 Personal Sampling Pump. A calibrated personal sampling pump whose flow rate can be determined to an accuracy of 5%. The sampling pump is protected from splashover or water condensation by an empty midget impinger positioned between the exit arm of the first bubbler and the pump.

6.1.4 Double distilled water.

6.1.5 Pipet, 15-mL or other suitable device for adding water to the bubbler.

6.1.6 Thermometer.

6.1.7 Barometer.

6.1.8 Stopwatch.

Spectrophotometer, capable of reading at 830 nm.

Matched glass cells or cuvettes, 1-cm path length.

Boiling water bath.

Assorted laboratory glassware; pipets, volumetric flasks, beakers, watchglasses.

7. Reagents

All reagents must be ACS reagent grade or better.

7.1 Distilled water.

7.2 Potasium dihydrogen phosphate stock solution. Dissolve 0.1389 g of potassium dihydrogen phosphate, KH_2PO_4, in distilled water and dilute to 1 liter (1 mL = 100 µg H_3PO_4).

7.3 Potassium dihydrogen phosphate working solution. Pipet 100 mL of the potassium dihydrogen phosphate stock solution into a 1 liter volumetric flask and dilute to the mark with distilled water.

7.4 Sodium molybdate solution. Dissolve 25.0 g of sodium molybdate, $Na_2MoO_4 \cdot 2H_2O$, in 10 N sulfuric acid and dilute to 1 liter with 10 N sulfuric acid.

7.5 Hydrazine sulfate solution. Dissolve 1.5 g of hydrazine sulfate, $N_2H_6SO_4$, in distilled water and dilute to 1 liter.

8. Procedure

Cleaning of Glassware. Contamination of glassware by detergents should be guarded against, especially when small amounts of phosphorus are being determined. Many detergents contain phosphates. Glassware that may have been cleaned with such detergents should be boiled in 1:1 hydrochloric acid and rinsed carefully with distilled water.

Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter holder, bubbler, and splashover trap in the line to minimize errors associated with uncertainties in the volume sampled.

Collection and Shipping of Samples

8.3.1 Assemble the filter in the two-piece filter holder and close firmly. The filter is supported by a stainless steel screen. Secure the filter holder together with tape or shrinkable band.

8.3.2 Pipet 15 mL of distilled water into the first midget bubbler, making sure the frit is covered.

8.3.3 Remove the filter holder plugs and attach the outlet of the holder to the inlet arm of the first midget bubbler using a short piece of flexible tubing. The outlet of this bubbler is connected by tubing to the inlet of a second, empty impinger (Section 6.1.3). The outlet of this second, empty impinger, or trap, is connected by a short piece of tubing to the pump's inlet. The trap is in a holder attached to the pump. Liquid which is collected in the trap must never be returned to the first bubbler. The bubblers must be maintained in a vertical position during sampling. If the solution in the bubbler spills into the trap, consider the sample void.

8.3.4 Air being sampled should not pass through any hose or tubing before entering the filter holder.

8.3.5 A sample size of 48 liters is recommended. Sample at a flow rate of 0.2 liter per minute for 240 minutes. The flow rate should be known with an accuracy of 5%.

8.3.6 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.7 Terminate sampling at the predetermined time and record sample flow rate, collection time, and ambient temperature and pressure. If pressure reading is not available, record the elevation. Also record the type of sampling pump used.

8.3.8 Remove the bubbler stem and tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Rinse the bubbler stem with 1-2 mL of distilled water and add the wash to the bubbler bottle. Seal the bubbler with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the bubblers should be tightly sealed to prevent leakage during shipping. If solution is spilled into the trap, consider the sample void. Be sure each bubbler bottom is properly labeled. Alternatively, the bubbler can be sealed by connecting the inlet to the outlet using Teflon tubing. If this is done, the bubbler tops must be sealed properly to prevent leakage.

8.3.9 Attempt to minimize sample spillage. Do not allow the solution level to drop below the top of the frit. Replace spilled solution with fresh distilled water. If spillage is not evidenced by liquid in the trap or in the tubing, evaporation is still probable. Use distilled water to bring the solution volume back up to 15 mL.

8.3.10 The filter should be removed from the filter holder and discarded. The holders should be cleaned and saved for future use.

8.3.11 With each batch of ten samples submit one bubbler containing 15 mL of distilled water from the same lot as that used for sample collection. This bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this bubbler as the blank.

8.4 Analysis of Samples

8.4.1 Transfer the contents of the bubbler quantitatively to a 50-mL volumetric flask.

8.4.2 Pipet 5 mL of the sodium molybdate solution and 2 mL of the hydrazine sulfate solution into the volumetric flask. Dilute to the mark with distilled water and shake well.

8.4.3 Immerse the volumetric flask in a boiling water bath for ten minutes. Remove and cool rapidly to room temperature.

8.4.4 Read the absorbance in a spectrophotometer at 830 nm against a reagent blank prepared in the same manner as the samples.

9. Calibration and Standardization

Pipet into six, 50-mL volumetric flasks, 0, 2.5, 5, 10, 15 and 20 mL of the potassium dihydrogen phosphate working solution.

Proceed as directed in Section 8.4.2.

Construct a calibration curve by plotting absorbance against the equivalent concentration of phosphoric acid in µg/50 mL.

10. Calculations

10.1 Determine from the calibration curve (Section 9.3) the number of µg phosphoric acid present in each sample. No volume corrections are needed since both the samples and standards are in 50 mL total volume. Determine the equivalent concentration of phosphorus pentachloride present in each sample.

$$\mu g\ PCl_5 = \mu g\ H_3PO_4 \times 2.125$$

10.2 Corrections for the "blank" sample, if any, must be made for each sample.

$$\mu g = \mu g\ \text{sample} \quad \mu g\ \text{blank}$$

where:

µg sample = µg found in sample bubbler

µg blank = µg found in blank bubbler

10.3 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$\text{Corrected Volume} = f \times t\left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f = sampling rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

= temperature during calibration of sampling pump (°K)

= temperature of air sampled (°K)

10.4 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\mu g\ PCl_5\ \text{(Section 10.2)}}{\text{Sampling Volume (liters)}}$$

10.5 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{208.3} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	=	pressure (mm Hg) of air sampled
T	=	temperature (°C) of air sampled
24.45	=	molar volume (liter/mole) at 25°C and 760 mm Hg
208.3		molecular weight (g/mole) of phosphorus pentachloride
760	=	standard pressure (mm Hg)
298	=	standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Phosphorus Pentachloride, No. S257, prepared under NIOSH Contract No. 210-76-0123.