PHOSPHINE

Method number:	1003

Target concentration:	0.3 ppm (0.42 mg/m^3, 12.3 nmol/L) TWA
OSHA PEL:	0.3 ppm (0.42 mg/m^3 12.3 nmol/L) TWA
ACGIH TLV:	0.3 ppm (0.42 mg/m^3 12.3 nmol/L) TWA
	1 ppm (1.4 mg/m^3, 40.9 nmol/L) STEL

Procedure:	Samples are collected by drawing workplace air, with personal sampling pumps, through sampling cassettes containing a glass fiber filter and a mercuric chloride-treated polyester filter. Samples are digested with sulfuric acid and analyzed by ICP-AES.

Recommended sampling time and sampling rate:	240 min at 1.0 L/min (240 L) TWA
	15 min at 2.0 L/min (30 L) STEL

Reliable quantitation limit:	32 ppb (45 µg/m^3)

Standard error of estimate at the target concentration:	5.52%

Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Methods Development Team. This method supercedes Method ID-180.

February 2000   Yihlin Chan
                                                                                                          Phil Giles

Methods Development Team
Industrial Hygiene Chemistry Division
OSHA Salt Lake Technical Center
Salt Lake City UT 84115-1802

1. General Discussion

   1.1   Background

      1.1.1   History

         With the application of phosphine in the manufacturing of semiconductors, the monitoring of workplace phosphine becomes more important than before. Phosphine has been analyzed by directly injecting sampled air onto a GC column. Both NPD[1] and FPD[2] have been used for detection. Wang et al. used gas sampling bags made of aluminum and polyester.[3]

         The NIOSH method uses sampling tubes containing mercuric cyanide-coated silica gel. Samples are oxidized with acidic permanganate and analyzed by colorimetry.[4] OSHA Method ID-180 for sampling workplace phosphine uses carbon bead coated with potassium hydroxide.[5] The analysis is based on the oxidation of the collected phosphine with hydrogen peroxide, and the determination of the resulting phosphite and phosphate by ion chromatography, but the method suffers from low recoveries.

         Greenfield et al. determined phosphine by passing air through a solution of mercuric chloride. Hydrogen chloride is liberated, causing a rise in conductance, proportional to the amount of phosphine absorbed.[6] They proposed the following reaction between phosphine and mercuric chloride:[7]

         $$PH_3 + 3HgCl_2 \rightarrow P(HgCl)_3 + 3HCl$$
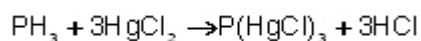
         Matsumura and co-workers coated silica gel with mercuric chloride and used it to sample phosphine.[8] Samples are oxidized with acidic permanganate and analyzed by colorimetry. The sampling capacity was 3 L with 0.3 ppm phosphine sampled at 0.3 L/min. The lower limit of quantitation was 0.054 ppm. The sampling time of 10 minutes is not suitable for TWA sampling, and the colorimetric determinations are cumbersome.

---

[1] Chughtai, M.; Pridham, P. N.; Cooke, M. Determination of phosphine by packed column gas chromatography with alkali flame ionisation detection. *Analytical Communications*, **1998**, 35, 109-111.

[2] Yang, G. and Dai, X. *Huanjing Baohu* (Beijin), **1994**, 59(12), 21-22.

[3] Wang, G.; Gao, Y.; Jiang, X.; Xiah, Y. Determination of phosphine in air by flame-photometric gas chromatography. *Weisheng Yanjiu*, **1994**, 23(2), 65-67; *Chem. Abstr*., 121, 116336.

[4] Phosphine, Method 6002, NIOSH Manual of Analytical Methods, Fourth Edition. **1994**.

[5] Ku, J. Phosphine in Workplace Atmospheres. *OSHA Analytical Method*, ID-180, **1988,** modified, **1991**.

[6] Greenfield, S.; Moule, H. A.; Perry, R. The Conductimetric Determination of Microgram Amounts of Phosphine in Air. *Analyst*, **1966**, 9, 10-14.

[7] They proposed this reaction based on the amount of hydrogen chloride generated. The precise nature of the phosphorus containing entity is not certain.

[8] Matsumura, Y.; Ono-Ogasawara, M.; Furuse, M. Adsorption Sampling of Phosphine and Some Other Semiconductor Material Gases. *Appl. Occup. Environ. Hyg*., **1993**, 8(4), 288-292. Determination of Phosphine by Adsorption Sampling with Modified Silica Gel and Colorimetry of Phosphine. *Industrial Health*, **1990**, 28, 175-184.

ICP-AES has been applied in the analysis of phosphorus. Hamalova and co-workers determined the phosphorus content of fertilizers using ICP-AES[9]. Ardis and Baker monitored the fertilizer plant effluents for phosphorus using ICP-AES[10]. Mortensen and co-workers collected phosphine in an impinger containing acidic permanganate solution and analyzed by ICP-AES.[11]

In the present method a mercuric chloride-treated polyester filter is used to capture phosphine and ICP-AES is used to analyze for the total phosphorus. A glass fiber filter is placed upstream to remove any phosphorus-containing particulate and aerosol.

1.1.2   Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

Phosphine is toxic by inhalation, but its effects are not completely understood. The chief effects are central nervous system depression and lung irritation. There may be pulmonary edema, dilation of the heart, and hyperemia of the visceral organs. Inhalation can cause coma and convulsions leading to death within 48 hours. However, most cases recover without after-effects. Chronic poisoning, characterized by anemia, bronchitis, gastrointestinal disturbances and visual, speech and motor disturbances, may result from continued exposure to very low concentrations.[12]

1.1.3   Workplace exposure

Two main uses for phosphine are in the preparation of semiconductors and as a fumigant.[13] Phosphine is commonly used in the electronics industry as an n-type dopant for silicon semiconductors, and to a lesser extent for the preparation of gallium-indium-phosphide devices. Phosphine generated *in situ* by the reaction of atmospheric moisture with pelletized calcium, aluminum, or magnesium phosphide is used as a fumigant in, for example, grain silos. Other uses of phosphine are as: polymerization initiator; condensation catalyst; chemical intermediate for phosphonium halides. Phosphine was not listed in either 1982 or 1972 NIOSH National Occupational Exposure Survey.[14] In the state of California for the period 1982-1992, there were reported 205 cases associated with exposure to phosphine/phosphides.[15]

---

[9] Hamalova, M.; Hodslavska, J.; Janos, P. Determination of Phosphorus, Potassium, and Magnesium in fertilizers by Inductively Coupled Plasma-Atomic Emission Spectroscopy and Comparison with Other Techniques. *J. AOAC International*, **1997**, 80(6), 1151-1155.

[10] Aardis., J. D.; Baker, A. M. Monitoring of Fertilizer Plant Effluents for Phosphorus, Sulfur, and Metals Using Inductively Coupled Plasma Emission Spectrometry. *J. Assoc. Off. Anal. Chem.*, **1989**, 72(5), 857-859.

[11] Mortensen, G.; Pedersen, B.; Rietz, B. ICP-AES and colorimetry as analytical tools for the determination of phosphorus containing compounds, including phosphine. *Analytical Letters*, **1989**, 22(7), 1791-1806.

[12] *Sax's Dangerous Properties of Industrial Materials*, 8th edition; Lewis, R. J., Ed.; Van Nostrand Reinhold: New York, 1992. Vol. 3, p 2783.

[13] Rickelton, W. A. Phosphine and Its Derivatives, In *Kirk Othmer Encyclopedia of Chemical Technology*, 4th edition; Kroschwitz, J. I., Howe-Grant, M., Eds,; John Wiley & Sons: New York, 1996; Vol. 18, pp 656-668.

[14] *OSHA Regulated Hazardous Substances - Industrial Exposure and Control Technologies*, Government Institutes, Inc., Rockville, MD, 1990.

[15] *NIOSH Alert: Preventing Phosphine Poisoning and Explosions during Fumigation;* DHHS (NIOSH) Publication No. 99-126; U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health; Cincinnati, 1999, p 3.

1.1.4   Physical properties and descriptive information[16]

CAS number:	7803-51-2
synonyms:	hydrogen phosphide; phosphorus trihydride
molecular formula:	PH_3
molecular weight:	34.00
boiling point:	-87.7 °C
melting point:	-133.8 °Cvapor pressure:3.14×10^4 mmHg at 20 °C
odor:	of decaying fish; of garlic
auto-ignition temperature:	38 °C (pure). Ignites readily at room temperature when other hydrides of phosphorus are present as impurities. Combines violently with oxygen and the halogens.
solubility:	soluble in ethyl alcohol and ether; slightly soluble in water (26 mL in 100 mL at 17 °C).
OSHA IMIS number:	2080[17]

This method was evaluated in part according to the OSHA SLTC "EVALUATION GUIDELINES FOR AIR SAMPLING METHODS UTILIZING CHROMATOGRAPHIC ANALYSIS"[18] and in part according to the Inorganic Method Development Guidelines[19]. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm are referenced to 25 °C and 101.3 kPa (760 mmHg).

1.2   Limit defining parameters

1.2.1   Detection limit of the analytical procedure

The detection limit of the analytical procedure is 0.088 µg/mL phosphorus. This is the concentration of phosphorus that will give a detector response that is significantly different from the response of a reagent blank. (Section 4.1)

1.2.2   Detection limit of the overall procedure

The detection limit of the overall procedure is 2.9 µg phosphorus per sample (10 ppb phosphine or 13 µg/m^3). This is the amount of phosphorus spiked on the sampler that will give detector response that is significantly different from the response of a sampler blank. (Sections 4.2)

1.2.3   Reliable quantitation limit

The reliable quantitation limit is 9.8 µg phosphorus per sample (32 ppb phosphine or 45 µg/m^3). This is the amount of phosphorus spiked on the sampler that will give detector response that is considered the lower limit for precise quantitative measurements. (Section 4.2)

[16] *Merck Index*, 10th Edition; Windholz, M. Ed.; Merck & Co.: Rahway, NJ, 1983.

[17] OSHA Salt Lake Technical Center, Chemical Sampling Information. http://www.osha-slc.gov/SLTC/ ChemSamp_data/ (accessed Dec 1999).

[18] Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. *EVALUATION GUIDELINES FOR AIR SAMPLING METHODS UTILIZING CHROMATOGRAPHIC ANALYSIS*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999.

[19] OSHA Salt Lake Technical Center, Inorganic Methods Evaluation Protocol. http://www.osha-slc.gov/SLTC/analytical_methods/html-methods/imeprotocol//imeprotocol.htm (accessed Oct 1999).

1.2.4 Instrument calibration

The standard error of estimate is 0.041 µg/mL phosphorus over the range of 1.0 to 8.0 µg/mL. This range corresponds to 0.25 to 2 times the target concentration. (Section 4.3)

1.2.5 Precision

The precision of the overall procedure at the 95% confidence level for the ambient temperature 17-day storage test (at the target concentration) from mercuric chloride-treated filters is ±10.8%. This includes an additional 5% for sampling pump variability. (Section 4.4)

1.2.6 Recovery

The recovery of phosphine from samples used in a 17-day storage test remained above 94.8% when the samples were stored at ambient temperature. (Section 4.5)

1.2.7 Reproducibility

Six samples collected from a controlled test atmosphere were submitted for analysis by the OSHA Salt Lake Technical Center. The samples were analyzed according to a draft copy of this procedure after 38 days of storage at ambient temperature. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.5. (Section 4.6)

2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in a manner that will not interfere with work performance or safety.

2.1 Apparatus

Samples are collected with 37-mm filter cassettes containing a glass fiber filter and a mercuric chloride-treated filter.[20]

---
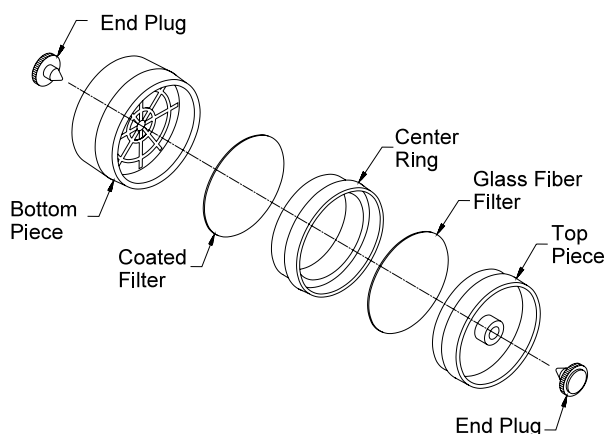
[20] The treated filter was prepared by the following procedure. Thirty-seven-millimeter-diameter round filters were cut from a piece of polyester non-woven fabric (polyester non-woven, ultra firm, Style #9260, Handler Textile Co., Consumer Product Div., 24 Empire Blvd., Moonachie, NJ 07074). The filters were washed (sonication) twice with methanol, three times with 10% nitric acid, twice with de-ionized water, twice with methanol, and dried. A solution of 4.0 g of mercuric chloride and a small amount of methyl orange in 40.0 mL of 95:5 (v/v) methanol/glycerol was prepared. **Caution**: Mercuric chloride is a poison and slightly volatile at ordinary temperature. Forty cleaned filters were placed on a clean glass plate and, using an Eppendorf pipet with a plastic tip, 0.95 mL of the mercuric chloride solution was applied to each filter. The filters were allowed to dry in a hood for 30 min. The treated filters were stored in a sealed container in a refrigerator.

Samples are collected using a personal sampling pump calibrated, with the sampling device attached, to within ±5% of the recommended flow rate.

2.2   Reagents

None required.

2.3   Technique

Remove the two end plugs from the cassette.

Attach the cassette to the sampling pump. Position the sampling pump, cassette and tubing so they do not impede work performance or safety.

Draw the air to be sampled directly into the inlet of the cassette. For personal sampling, the air being sampled is not to be passed through any hose or tubing before entering the sampling cassette.

After sampling for the appropriate time, remove the cassette and replace the two end plugs. Seal each sample end-to-end with an OSHA-21 form.

Submit at least one blank sample with each set of samples. Handle the blank sampler in the same manner as the other samples except draw no air through it.

Record sample air volume (liters), sampling time (minutes) and sampling rate (L/min) for each sample, along with any potential interferences on the OSHA-91A form.

Submit the samples to the laboratory for analysis as soon as possible after sampling.

2.4   Sampler capacity (Section 4.7)

The sampling capacity was tested by sampling a dynamically generated test atmosphere of phosphine at 3.8 times the target concentration (46.8 nmol/L, 1.59 mg/m^3 or 1.34 ppm) at an absolute humidity of 16.3 milligrams of water per liter of air (74.9% relative humidity at 24 °C). The samples were collected at 1.0 L/min. The 5% breakthrough sampling time was determined to be 335 min. The 5% breakthrough was not reached in 6 hours when tested at two times the target concentration. When tested at 113.4 nmol/L (2.8 times the ACGIH STEL) and at a flow rate of 2.0 L/min, the 5% breakthrough sampling time was determined to be 40 min.

2.6   Recommended sampling time and sampling rate

Sample for up to 240 min at 1.0 L/min (240 L) to collect TWA (long-term) samples.

Sample for 15 min at 2.0 L/min (30 L) to collect short-term samples.

When short-term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit is 0.36 mg/m^3 (10.5 nmol/L, 0.26 ppm) when 30 L are collected.

2.7   Interferences, sampling (Section 4.8)

The collection efficiency was above 94.6% when mercuric chloride-treated filters were used to sample a test atmosphere containing the target concentration of phosphine and having an absolute humidity of 4.6 milligrams of water per liter of air (22.2% relative humidity at 23.3 °C).

The collection efficiency was above 75.0% when mercuric chloride-treated filters were used to sample a test atmosphere containing 0.08 times the target concentration of phosphine and having an absolute humidity of 15.6 milligrams of water per liter of air (64.1% relative humidity at 26.0 °C).

The collection efficiency was above 99.6% when the samplers, whose front glass fiber filter had been spiked with 2.4 mg of ammonium phosphate dibasic,[21] were used to sample a test atmosphere containing one times the target concentration of phosphine and having an absolute humidity of 15.5 milligrams of water per liter of air (70.9% relative humidity at 24.1 °C). The average collection efficiency was 101.1% for the control samples.

The collection efficiency was above 96.7% when the samplers, whose front glass fiber filter had been spiked with 0.214 mg of DDVP,[21] were used to sample a test atmosphere containing one times the target concentration of phosphine and having an absolute humidity of 15.5 milligrams of water per liter of air (70.9% relative humidity at 24.1 °C). The average collection efficiency was 101.1% for the control samples.

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan[22]. Avoid skin contact and inhalation of all chemicals. Review appropriate MSDSs before beginning work.

3.1   Equipment

3.1.1   Inductively coupled plasma-atomic emission spectrometer (ICP-AES). A Perkin-Elmer Optima 3000 DV, with its accessories including auto-sampler, peristaltic pumps, and mass flow controller, was used in this evaluation. The software controls the instrument and provides the analytical results.

3.1.2   Borosilicate glass Phillips beakers, 125-mL.

3.1.3   Borosilicate glass volumetric flasks, 25-mL,

3.1.4   Hot plate.

3.2   Reagents

3.2.1   Sulfuric acid, reagent grade. Sulfuric acid, 96.5%, purchased from JT Baker was used (Lot 15055).

3.2.2   Hydrogen peroxide, 30%. Hydrogen peroxide, 30%, was purchased from Mallinckrodt.

3.2.3   De-ionized water.

3.2.4   Phosphorus standard, 1000 µg/mL. Single element phosphorus standard, 1000 µg/mL, was purchased from SPEX Industries (Edison, NJ) and from CPI International (Santa Rosa, CA).

3.2.5.   Nitric acid.

---

[21] Ammonium phosphate and DDVP (2,2-dichlorovinyl dimethyl phosphate) were selected to represent residual fertilizers and semi-volatile organo-phosphorus pesticides that may possibly interfere with the sampling for phosphine during a grain fumigation operation. DDVP has a vapor pressure of 0.012 torr (1.6 Pa) at 20 °C. *(Documentation of the Threshold Limit Values and Biological Exposure Indices*, Sixth Edition; American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1991; p.446.)

[22] Occupational Exposure to Hazardous Chemicals in Laboratories. *Code of Federal Regulations*, Part 1910.1450, Title 29, 1998.

3.3   Standard preparation

3.3.1   Working standard, 10 µg/mL phosphorus (10 ppm P). Pipet 1.00 mL of 1000 µg/mL phosphorus stock solution into a 100-mL volumetric flask. Add about 50 mL of de-ionized water. Add 8 mL of concentrated sulfuric acid. Allow the solution to cool. Add de-ionized water to the mark.

3.3.2   Prepare a reagent blank in a 100-mL volumetric flask by adding 8 mL of sulfuric acid to about 50 mL of de-ionized water, allowing it to cool, and adding de-ionized water to the mark.

3.4   Sample preparation

Caution: Mercuric chloride is a "violent poison" and "slightly volatile at ordinary temperature".[23] It has a vapor pressure of 13 Pa (0.1 torr) at 100 °C.[24] Handle samples in a hood.

Clean the insides of the 125-mL Phillips beakers by refluxing 1:1 nitric acid using a hot plate in a ventilated hood. Carefully pour the used 1:1 nitric acid into an appropriate labeled container. Allow the beakers to cool, then rinse several times with de-ionized water. Using a forceps, place sample filters in separate labeled and washed Phillips beakers. Discard the glass fiber filter.

Add 2 mL of concentrated sulfuric acid to each beaker.

Heat the beakers on a hot plate for approximately 10 minutes. The solutions should become dark and then light brown.

Add a few drops of 30% hydrogen peroxide until each solution becomes colorless. Remove the beakers from the hot plate and allow to cool.

Quantitatively transfer the solutions into 25-mL volumetric flasks using de-ionized water. Add de-ionized water to the mark.

3.5   Analysis

Follow the standard operating procedure for ICP-AES.   There   are   four   available wavelengths for phosphorus determination: 178.221, 177.433, 213.616, and 214.918 nm. The wavelength of 178.221 nm was used in this evaluation. The results from the other three wavelengths are useful for confirmation. Calibrate with the 10 µg/mL phosphorus standard   and   the   reagent   blank.   The instrument   software   allows   for   taking   a specified number of readings and calculating the averages.
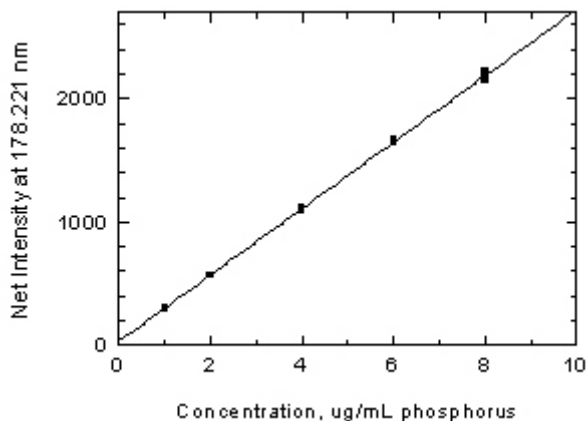

Figure 3.5. Calibration curve of phosphorus. (Y = 268.9X + 31.95).

[23] *Merck Index*, 10th Edition; Windholz, M. Ed.; Merck & Co.: Rahway, NJ, 1983, p 839.

[24] Nowak, M.; Singer, W. Mercury Compounds. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edition; Kroschwitz, J. I.; Howe-Grant, M., Eds; John Wiley & Sons: New York, NY, 1995; Volume 16, p 232.

ICP operating parameters:

number of replicates: 2
integration times: minimum: 5.00 sec
    maximum: 20.00 sec
plasma flow: 15 L/min
auxiliary plasma flow: 0.5 L/min
nebulizer gas flow: 0.60 L/min
power: 1450 watts
viewing height: 15 mm
plasma view: radial or axial

For the calibration curve presented in Figure 3.5, three readings were taken and the individual data points were plotted.

3.6   Interferences (analytical)

Copper and iron, when present in large amounts, may interfere with phosphorus detection at 213.616 and 214.914 nm. The ICP software allows for the correction of spectral interferences. Consult the instrument manual for inter-element corrections.

3.7   Calculations

The concentration of phosphorus for the sample is obtained from the appropriate calibration curve in terms of micrograms phosphorus per milliliter. This concentration is then corrected by subtracting the concentration of the blank. The air concentration is calculated using the following formulas.

$$C_M = \frac{(C_P)(V_d)(34.00)}{(V)(30.97)}$$

where C_M is concentration by weight (mg/m^3)
    C_p is micrograms phosphorus per milliliter
    V is liters of air sampled
    V_d is the final volume (mL) to which the sample is diluted
    34.00 is the molecular weight of phosphine (g/mol)
    30.97 is the atomic weight of phosphorus (g/mol)

$$C_V = \frac{(24.46)(C_M)}{34.00}$$

where C_V is concentration by volume (ppm)
    24.46 is molar volume at 25 °C (L/mol)
    C_M is concentration by weight (mg/m^3)
    34.00 is the molecular weight of phosphine (g/mol)

4. Backup Data

General background information about the determination of detection limits and precision of the overall procedure is found in the "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"[25]. The Guidelines define analytical parameters, specific laboratory tests, statistical calculations and acceptance criteria.

---

[25] Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. *EVALUATION GUIDELINES FOR AIR SAMPLING METHODS UTILIZING CHROMATOGRAPHIC ANALYSIS*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999.

4.1   Detection limit of the analytical procedure (DLAP)

A 10 µg/mL phosphorus standard and a reagent blank were analyzed ten times and the data obtained were used to determine the DLAP according to the following formula.[26] At 178.221 nm, the 10 µg/mL standard gave an average intensity of 2717.8. The reagent blank gave an average intensity of 25.8 and a standard deviation of 7.87. DLAP was calculated to be 0.088 µg/mL phosphorus.

$$D_L = \frac{k(S_{dblk})(C_{std})}{(I_{std} - I_{blk})}$$

where D_L is detection limit
k is a constant, equals 3
S_{dblk} is the standard deviation of the reagent blank
C_{std} is the concentration of the standard
I_{std} is the intensity of the standard
I_{blk} is the intensity of the blank

4.2   Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)

The DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of phosphorus, such that the highest sampler loading was 20 µg/sample. This is the amount spiked on a sampler that would produce a peak approximately 10 times the response of a sample blank. These spiked samplers and the sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate and the slope) for the calculation of the DLOP. Values of 10.55 and 10.34 were obtained for the slope and standard error of estimate respectively. The DLOP was calculated to be 2.94 µg phosphorus per sample (9.67 ppb phosphine, 13.4 µg/m^3).

Table 4.2
Detection Limit of the Overall Procedure

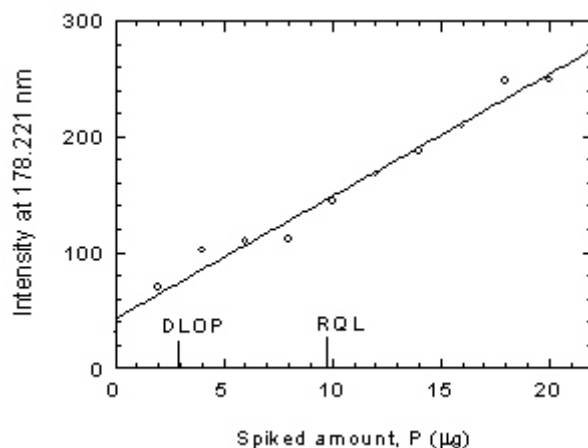| mass per sample (µg phosphorus)	intensity at 178.221 nm
0	34.1
2	69.8
4	102.3
6	109.5
8	111.5
10	144.1
12	167.8
14	187.2
16	209.3
18	248.1
20	249.3

Figure 4.2. Plot of data to determine the DLOP/RQL. (Y = 10.55X + 42.91).

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained for the calculation of the DLOP, providing 75% to 125% of the analyte is recovered. The RQL is 9.80 µg phosphorus per sample (1.32 nmol/L, 32.2 ppb phosphine, 44.8 µg/m^3)   Recovery at this concentration is 95.9%.

4.3   Instrument calibration

[26] OSHA Salt Lake Technical Center, Inorganic Methods Evaluation Protocol. http://www.osha-slc.gov/SLTC/analytical_methods/html-methods/imeprotocol//imeprotocol.htm (accessed Oct 1999).

The standard error of estimate was determined from the linear regression of data points from standards over a range that covers 0.25 to 2 times the target concentration. A calibration curve was constructed and shown in Section 3.5 from the three readings of five standards. A standard error of estimate of 15.38 and a slope of 268.7 mL/µg were obtained for the curve. The standard error of estimate of the calibration is calculated to be 0.0572 µg/mL phosphorus.

Table 4.3.
Instrument Calibration

standard concn (µg/mL P)	net intensity at 178.221 nm			average
1.00	303.5	305.4	298.4	302.4
2.00	570.6	567.9	568.7	569.0
4.00	1086.5	1104.3	1117.3	1102.7
6.00	1663.5	1646.6	1647.0	1652.4
8.00	2152.3	2173.6	2216.5	2180.8

4.4   Precision (overall procedure)

The precision at the 95% confidence level is obtained by multiplying the standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). In Section 4.5, 95% confidence intervals are drawn about their respective regression lines in the storage graph figures. The precision of the overall procedure of ±10.8% was obtained from the standard error of estimate of 5.52% in Figure 4.5.1.

4.5   Storage test

Storage samples for phosphine were prepared by collecting samples from a controlled test atmosphere using the recommended sampling conditions. The concentration of phosphine was at the target concentration with an absolute humidity of 14.8 milligrams of water per liter of air (86.3% at 19.9 °C).[27] Thirty-three storage samples were prepared. Three samples were analyzed on the day of generation. Fifteen of the samples were stored at reduced temperature (4 °C) and the other fifteen were stored in a closed drawer at ambient temperature (about 22 °C). At 3-4 day intervals three samples were selected from each of the two sets and analyzed.

Table 4.5
Storage Test for Phosphine

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	96.7	93.7	94.3	96.7	93.7	94.3
4	96.1	95.0	96.7	98.9	93.3	98.1
7	90.8	94.9	93.7	92.4	93.7	96.2
10	92.2	97.3	99.9	95.6	97.8	95.9
14	95.9	98.5	95.4	99.7	101.3	98.4
17	97.1	96.7	92.3	94.8	94.0	95.4

---

[27] The test atmosphere was generated by diluting a stream of certified 524.6 ppm phosphine in nitrogen (at a flow rate of 25.5 mL/min) with an air stream (at 38.38 L/min) from a Miller-Nelson humid air generator. The temperature was 19.9 °C and the barometric pressure was 86.8 kPa (651.3 mmHg). The phosphine concentration was calculated to be 0.348 ppm or 12.4 nmol/L.
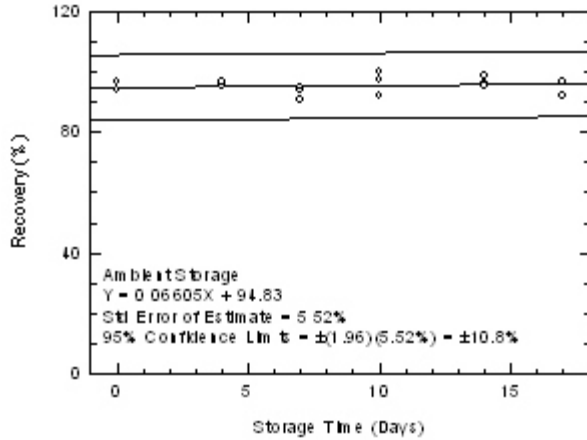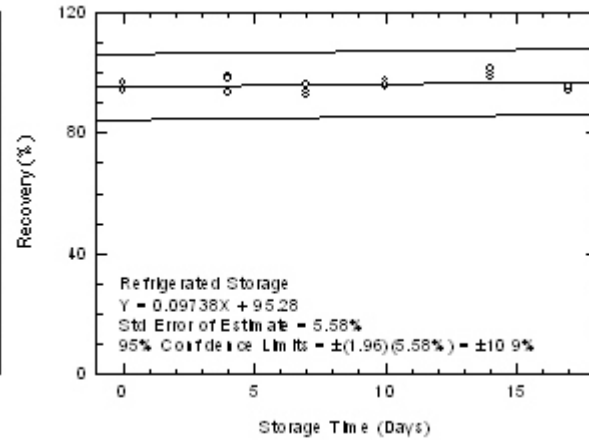
Figure 4.5.1. Ambient storage test for phosphine.

Figure 4.5.2. Refrigerated storage test for phosphine.

4.6   Reproducibility

Six samples were collected from a controlled test atmosphere similar to that which was used in the collection of the storage samples. The samples were submitted to the OSHA Salt Lake Technical Center for analysis.   The samples were analyzed after being stored for 38 days at ambient temperature.   No sample result for phosphine had a deviation greater than the precision of the overall procedure determined in Section 4.4.

Table 4.6
Reproducibility Data for Phosphine on Mercuric Chloride-Treated Filter

theoretical concentration (µg/L)	recovered amount (µg/mL P)	air volume (L)	concentration (µg/L)	recovery (%)	deviation (%)
0.4055	3.350	245.0	0.3753	92.6	-7.4
0.4055	3.339	242.9	0.3773	93.0	-7.0
0.4055	3.331	242.3	0.3773	93.0	-7.0
0.4055	3.247	241.7	0.3687	90.9	-9.1
0.4055	3.452	242.0	0.3915	96.5	-3.5
0.4055	3.403	245.0	0.3812	94.0	-6.0

4.7   Sampler capacity

The sampling capacity of the mercuric chloride-treated filter was tested by sampling from a dynamically generated test atmosphere of phosphine (46.8 nmol/L or 1.34 ppm at Salt Lake City) with an absolute humidity of 16.3 milligrams of water per liter of air (74.9% relative humidity at 24 °C) using two samplers connected in series. Three sets of samples were collected at 1.0 L/min. At 30-minutes intervals the downstream sampler was replaced with a fresh one. The 5% breakthrough was seen at 335 L of sampled air. No breakthrough was seen in 6 hours when the test was conducted at 26.2 nmol/L (0.738 ppm at Salt Lake City). The recommended sampling time is 4 h.

When tested at 113.4 nmol/L (2.8 times the ACGIH STEL TLV) and at a flow rate of 2.0 L/min, the 5% breakthrough time was found to be 40 min. The recommended short term sampling time and flow rate are 15 min and 2.0 L/min.

T-1003-FV-01-0002-M

Table 4.7.1
Breakthrough of Phosphine with Mercuric Chloride-
Treated Filter at 46.8 nmol/L and at 1 L/min

| test no.	sampling time (min)	air vol (L)	downstream concn (nmol/L)	break- through (%)
1	0 -130	65.6	0.80	1.7
	130 - 206	169.5	0.61	1.3
	206 - 240	225.0	0.05	0.1
	240 - 270	257.3	0.01	0.0
	270 - 302	288.6	0.15	0.3
	302 - 330	318.8	1.89	4.0
	330 - 360	348.1	4.27	9.1
2	0 -130	65.0	0.74	1.6
	130 - 206	168.0	Outlier	-
	206 - 240	223.0	1.39	3.0
	240 - 270	255.0	0.61	1.3
	270 - 302	286.0	1.62	3.4
	302 - 330	316.0	1.35	2.9
	330 - 360	345.0	2.97	6.3
3	0 -130	64.6	0.54	1.1
	130 - 206	166.9	0.50	1.1
	206 - 240	221.5	1.46	3.1
	240 - 270	253.3	0.62	1.3
	270 - 302	284.1	0.62	1.3
	302 - 330	313.9	1.50	3.2
	330 - 360	342.7	1.85	4.0
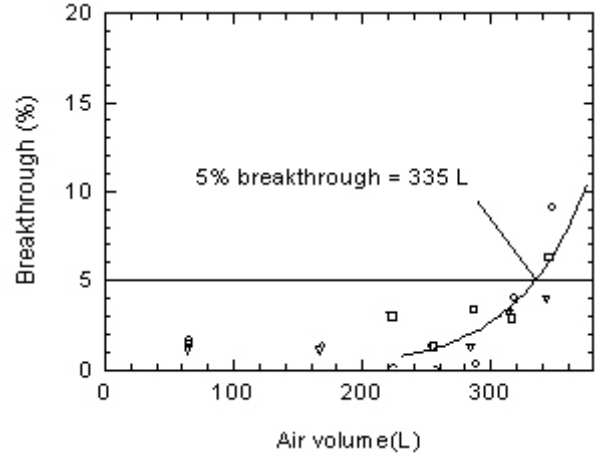
Figure 4.7.1. Five percent breakthrough air volume for phosphine at 46.8 nmol/L (3.8 times the target concentration) and a flow rate of 1.0 L/min.

T-1003-FV-01-0002-M

Table 4.7.2
Breakthrough of Phosphine with Mercuric Chloride-
Treated Filters
at 2 L/min and at 113.4 nmol/L (3.857 mg/m^3)

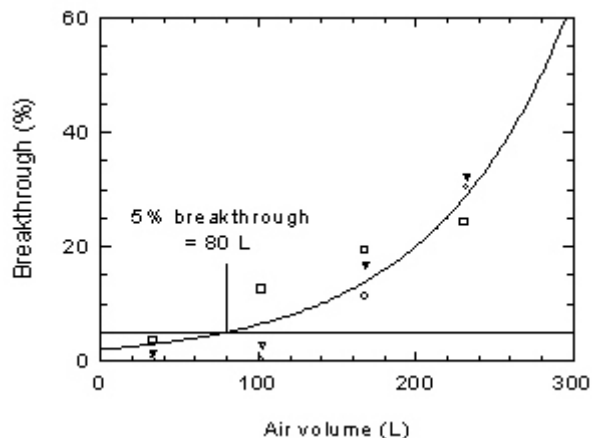| test no.	sampling time (min)	air vol (L)	downstream concn (nmol/L)	break-through (%)
1	0 - 33	32.8	4.1	3.6
	33 - 69	101.3	14.3	12.6
	69 - 99	166.8	22.1	19.5
	99 -133	230.4	27.6	24.3
2	0 - 33	33.0	0.3	0.2
	33 - 69	102.0	0.1	0.1
	69 - 99	168.0	12.8	11.3
	99 - 133	232.0	34.3	30.3
3	0 - 33	33.1	1.4	1.3
	33 - 69	102.2	3.3	2.9
	69 - 99	168.3	19.0	16.8
	99 -133	232.5	36.6	32.3

Figure 4.7.2. Five percent breakthrough air volume for phosphine at 113.4 nmol/L (2.8 times the ACGIH STEL TLV) and at a flow rate of 2.0 L/min.

4.8   Interferences (sampling)

Low humidity

The ability of the mercuric chloride-treated filter to collect phosphine from a relatively dry atmosphere was tested by sampling an atmosphere containing 12.2 nmol/L (one times the target concentration) of phosphine at an absolute humidity of 4.6 milligrams of water per liter of air (22.2% relative humidity at 23.3°C). Six samples were collected from the test atmosphere at 1.0 L/min for 240 minutes. All of the samples were immediately analyzed. The samples had collected 94.6%, 94.9%, 96.8%, 98.5%, 95.0%, and 103.3% of theoretical.

Low concentration

The ability of the mercuric chloride-treated filter to collect phosphine at low concentrations was tested by sampling an atmosphere containing 1.31 nmol/L (0.11 1times the target concentration) of phosphine at an absolute humidity of 14.0 milligrams of water per liter of air (63.8% relative humidity at 24.2 °C). Six samples were collected from the test atmosphere at 1.0 L/min for 240 min. The samples were immediately analyzed. The samples had collected 87.2%, 88.8%, 81.2%, 84.4%, 83.8%, and 82.4% of theoretical.

Interference

The ability of a mercuric chloride-treated filter coupled with the glass fiber filter to collect phosphine was tested when other potential interferences are present. Twelve samplers were used. The glass fiber filter of the three samplers were spiked with 100 µL of 24 mg/mL ammonium phosphate dibasic. The glass fiber filter of the next three samplers were spiked with 100 µL of 2.14 mg/mL DDVP in toluene. The remaining six samplers were used as controls. They were used to sample an atmosphere containing 11.9 nmol/L (0.97 times the target concentration) of phosphine at an absolute humidity of 15.5 milligrams of water per liter of air (70.9% relative humidity at 24.1°C) at 1.0 L/min for 240 minutes.   All of the samples were immediately analyzed. The samplers with ammonium phosphate on the glass fiber filter had collected an average of 100.7% of theory. The three samplers with DDVP on the glass fiber filter had collected an average of 99.9% of theory. The six control samplers had collected an average of 101.1% of theory.

Table 4.8.1
Interference Tests for Phosphine

interference, amount placed on the front filter	recovery (%)			average recovery (%)
ammonium phosphate, dibasic, 2.4 mg	101.2	99.6	101.4	100.7
DDVP, 0.214 mg	102.7	96.7	100.2	99.9
control	93.3	105.7	103.1	101.1
	102.1	100.4	102.1	

Shelf life of the coated filter

The shelf life of the mercuric chloride-treated filter was tested by comparing the sampling recoveries of the 112-day-old filters with the 6-day-old ones. Three samplers from each set were used to sample an atmosphere containing 12.9 nmol/L (1.05 times the target concentration) of phosphine at an absolute humidity of 15.1 mg of water per liter of air (72.2% relative humidity at 23.3°C) at 1.0 L/min for 245 minutes. The average recovery from the 112-day-old filters was 83.5%. The average recovery from the 6-day-old filters was 93.4%. The filter is good for three months.

Table 4.8.2
Comparison of Old and New Filters

age of filters	recovery (%)			average (%)
112 days	80.2	92.3	77.9	83.5
6 days	94.3	94.5	91.3	93.4

T-1003-FV-01-0002-M