



# PHOSPHINE

6002

PH<sub>3</sub> MW: 34.00 CAS: 7803-51-2 RTECS: SY7525000

METHOD: 6002, Issue 3

EVALUATION: FULL

Issue 1: 15 August 1994  
Issue 3: 20 October 2015

OSHA: 0.3 ppm (0.4 mg/m<sup>3</sup>)  
NIOSH: 0.3 ppm (0.4 mg/m<sup>3</sup>); 1 ppm (1 mg/m<sup>3</sup>) STEL

PROPERTIES: Gas, BP 87.8 °C; vapor density 1.17 (air = 1); spontaneously flammable in air if diphosphane is present

SYNONYMS: Hydrogen phosphide; phosphorus hydride; phosphorated hydrogen; phosphorus trihydride

SAMPLING	MEASUREMENT
<p><b>SAMPLER:</b> SORBENT TUBE (mercuric cyanide-coated silica gel, 300 mg/150 mg)</p> <p><b>FLOW RATE:</b> 0.01 L/min to 0.2 L/min</p> <p><b>VOL-MIN:</b> 1 L @ 0.3 ppm <b>-MAX:</b> 16 L</p> <p><b>SHIPMENT:</b> Routine</p> <p><b>SAMPLE STABILITY:</b> 7 d @ 25 °C</p> <p><b>BLANKS:</b> 2 to 10 field blanks per set</p>	<p><b>TECHNIQUE:</b> UV-VIS SPECTROMETER</p> <p><b>ANALYTE:</b> Phosphate</p> <p><b>EXTRACTION:</b> 10 mL hot (65 °C to 70 °C) acidic permanganate reagent solution</p> <p><b>DETECTOR:</b> UV @ 625 nm</p> <p><b>CALIBRATION:</b> Standard solutions of potassium dihydrogen phosphate (1.00 mL contains phosphorus equivalent to 49.94 µg of phosphine)</p> <p><b>RANGE:</b> 0.3 µg to 10 µg per sample [2]</p> <p><b>ESTIMATED LOD:</b> 0.1 µg per sample [1]</p> <p><b>PRECISION (<math>\hat{S}_r</math>):</b> 0.074 @ 2.6 µg to 17.4 µg per sample [2]</p>
ACCURACY	
<p><b>RANGE STUDIED:</b> 0.195 mg/m<sup>3</sup> to 0.877 mg/m<sup>3</sup> [1] (16 L samples)</p> <p><b>BIAS:</b> 0.4%</p> <p><b>OVERALL PRECISION (<math>\hat{S}_{rr}</math>):</b> 0.091 @ 2.64 µg to 17.41 µg per sample [2]</p> <p><b>ACCURACY:</b> ±17.6%</p>	

APPLICABILITY: The working range is 0.013 ppm to 0.6 ppm (0.02 mg/m<sup>3</sup> to 0.9 mg/m<sup>3</sup>) for a 16 L air sample.

INTERFERENCES: The colorimetric determination of phosphate is subject to interference by any species that also forms a molybdate complex under these conditions; possible interfering species include phosphorus trichloride and phosphorus pentachloride vapors and organic phosphorus compounds.

OTHER METHODS: This revises NIOSH method S332 [2]. OSHA method 1003, "Phosphine" [3], employing a mercuric chloride-treated polyester filter used to capture phosphine and ICP-AES to analyze for the total phosphorus, may be used as an alternative method.

**REAGENTS:**

1. Potassium dihydrogen phosphate, anhydrous, ACS reagent grade.
2. Sulfuric acid,\* concentrated, ACS reagent grade.
3. Ammonium molybdate tetrahydrate.
4. Ferrous ammonium sulfate, anhydrous.
5. Potassium permanganate.\*
6. Stannous chloride.
7. Glycerol.
8. Toluene.\*
9. Isobutanol.\*
10. Methanol.\*
11. Water, deionized or distilled.
12. Mercuric cyanide.\*
13. Standard phosphate solution. Dissolve 200 mg anhydrous potassium dihydrogen phosphate in distilled water and dilute to 1 L (1.00 mL contains phosphorus equivalent to 49.94 µg of phosphine).
14. Molybdate solution. Dissolve 49.4 g of ammonium molybdate tetrahydrate and 112 mL concentrated sulfuric acid in distilled water and dilute to 1 L.
15. Alcoholic sulfuric acid solution. Add 50 mL of concentrated sulfuric acid to 950 mL methanol.
16. Toluene-isobutanol solvent. Mix equal volumes of toluene and isobutanol.
17. Ferrous solution. Dissolve 7.9 g anhydrous ferrous ammonium sulfate and 1 mL concentrated sulfuric acid in distilled water and dilute to 100 mL.
18. Stannous chloride solution. Dissolve 0.4 g stannous chloride in 50 mL glycerol (heat to dissolve).
19. Acidic permanganate solution. Dissolve 0.316 g potassium permanganate and 6 mL concentrated sulfuric acid in distilled water and dilute to 1 L.
20. Mercuric cyanide solution.\* Dissolve 2 g mercuric cyanide in 100 mL water.

\*See SPECIAL PRECAUTIONS.

**EQUIPMENT:**

1. Sampler: Sorbent tube, silica gel (mercuric cyanide), 300 mg/150 mg sorbent, 40/60 mesh; or, glass tube 12 cm long, 6 mm O.D., 4 mm I.D., flame-sealed ends with plastic caps, with two sections of mercuric cyanide-treated silica gel (45/60 mesh), (front = 300 mg, back = 150 mg), separated and retained by silylated glass wool plugs. (See APPENDIX.)
2. Personal sampling pump, 0.01 L/min to 0.2 L/min, with flexible polyethylene or PTFE tubing.
3. Spectrometer capable of measuring absorbance or transmittance at 625 nm.
4. Two matched 5 cm absorbance cells, silica, with tight fitting caps.
5. Separatory funnel, 125 mL.
6. Beakers, 50 mL.
7. Pipets, 0.2 mL, 10 mL, and 25 mL, and other convenient sizes to make standard dilutions.
8. Volumetric flasks, 10 mL, 25 mL, 100 mL, and 1000 mL.
9. Water bath (maintained at 65 °C to 70 °C).
10. Graduated cylinders, glass, 10 mL.
11. Syringes, 0.5 mL and 1.0 mL.
12. Balance.
13. Thermometer.
14. Stopwatch.
15. Barometer.

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**SPECIAL PRECAUTIONS:** Caution should be exercised when preparing the sampling media because mercuric cyanide is toxic by inhalation, ingestion, and skin contact. Contact of mercuric cyanide with acid will produce hydrogen cyanide gas. Concentrated sulfuric acid is highly corrosive. All work with these compounds should be performed in a hood. Use proper protective clothing including gloves, safety glasses, and laboratory coat. Potassium permanganate is a strong oxidizer with risk of fire and explosion upon contact with combustible substances and reducing agents. Toluene, isobutanol, and methanol are flammable.

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**SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break the ends of the silica gel tubes to provide an opening of at least one half the internal diameter of the tube. Attach the silica gel tube to the sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 L/min and 0.2 L/min for a total sample size of 1 L to 16 L.
4. Seal tubes with plastic (not rubber) caps.

**SAMPLE PREPARATION:**

5. Place front and back sorbent sections in separate 50 mL beakers.
6. Add 10 mL of acidic permanganate solution to each beaker. Place in a water bath maintained at 65 °C to 70 °C for 90 min.
7. Decant the acidic permanganate solution into a 10 mL volumetric flask, and dilute to volume with distilled water.
8. Wash the silica gel twice with 3 mL portions of distilled water and decant the contents into another 10 mL volumetric flask containing 1 mL of ferrous solution. Dilute to volume with distilled water.
9. Add the contents of both 10 mL volumetric flasks (extract and washings) to a 125 mL separatory funnel.
10. Add 7.5 mL of molybdate reagent and 25 mL of toluene-isobutanol solvent to the funnel. Shake funnel for 60 s. Let the separatory funnel stand for 60 s to allow the aqueous and nonaqueous layers to separate. Discard the lower (aqueous) layer.
11. Pipet 10 mL of the nonaqueous layer into a 25 mL volumetric flask containing 10 mL of the alcoholic sulfuric acid solution.

**CALIBRATION AND QUALITY CONTROL:**

12. Calibrate daily with at least six working standards.
  - a. Add 10 mL of acidic permanganate solution and 1 mL of ferrous reagent to a 125 mL separatory funnel.
  - b. Add 2 µL to 400 µL of the standard phosphate solution to cover the range 0.1 µg to 10 µg of phosphine. Add 8 mL to 9 mL of water to make the total volume of the solution (permanganate solution, ferrous solution, phosphate solution and water) equal to 20 mL. Prepare at least six calibration standards and a blank containing no phosphate.
  - c. Add 7.5 mL of molybdate reagent and 25 mL of toluene-isobutanol solvent to the funnel. Shake funnel for 60 s. Let the separatory funnel stand for 60 s to allow the aqueous and nonaqueous layers to separate. Discard the lower (aqueous) layer. (step 10)
  - d. Pipet 10 mL of the nonaqueous layer into a 25 mL volumetric flask containing 10 mL of the alcoholic sulfuric acid solution. (step 11)
  - e. Analyze with samples and blanks (steps 15, 16, 17, and 18).
  - f. Prepare a calibration graph (absorbance versus µg of phosphine added).
13. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
  - a. Remove and discard back sorbent section of a media blank sampler.
  - b. Inject a known amount (20 µL to 400 µL) of standard phosphate solution directly onto front sorbent section with a microliter syringe.
  - c. Cap the tube. Allow to stand overnight.
  - d. Desorb (steps 6, 7, and 8) and analyze with working standards (steps 15, 16, 17, and 18).
  - e. Prepare a graph of DE vs. µg recovered.

14. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

## MEASUREMENTS

15. Turn on the spectrophotometer and allow sufficient time for warmup. Adjust the wavelength to 625 nm and set the zero and 100% transmittance scale using 5 cm cells filled with distilled water. Check these settings prior to making any measurement to check on instrument drift.

**NOTE: Steps 16, 17, and 18 must be performed within 1 min.**

16. Add 0.5 mL (25 drops) of stannous chloride reagent and dilute to volume using alcoholic sulfuric acid solution. Mix thoroughly.
17. Transfer the sample into a 5 cm cell and stopper immediately.
18. Measure the absorbance or transmittance using water as a blank.

## CALCULATIONS:

19. Determine mass,  $\mu\text{g}$  (corrected for DE), of phosphine found in the sample front ( $W_f$ ) and back ( $W_b$ ) sorbent sections, and in the average media blank front ( $B_f$ ) and back ( $B_b$ ) sorbent sections.

NOTE: If  $W_f > W_b / 10$ , report breakthrough and possible sample loss.

20. Calculate concentration,  $C$ , of phosphine in the air volume sampled,  $V$  (L).

$$C = \frac{W_f + W_b - B_f - B_b}{V}, \mu\text{g/L or mg/m}^3.$$

## EVALUATION OF METHOD:

This method was validated over the range 0.195 mg/m<sup>3</sup> to 0.877 mg/m<sup>3</sup> at 19 °C and 102.0 kPa (765.3 mmHg) using 16 L samples [1]. Desorption efficiency must be determined over the range used. The upper range of the method depends on the adsorptive capacity of the mercuric cyanide-treated gel. This capacity may vary with the concentration of phosphine and other substances in the air. When an atmosphere at 90% relative humidity containing 0.957 mg/m<sup>3</sup> of phosphine was sampled at a flow rate of 0.2 L/min, breakthrough was determined to occur at a sample volume of 20.75 liter (capacity = 19.86  $\mu\text{g}$  phosphine).

## REFERENCES:

- [1] NIOSH [1979]. Backup data report: phosphine, No. S332. In: Ten NIOSH analytical methods, set 7. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health, available as accession No. PB84-243534 from NTIS [www.ntis.gov]. Unpublished.
- [2] NIOSH [1979]. Phosphine: Method S332. In: Taylor DG, ed. NIOSH manual of analytical methods. 2nd ed. Vol. 5. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 79-141, available as accession No. PB83-105445 from NTIS [www.ntis.gov].
- [3] OSHA [2000]. Phosphine: OSHA Method 1003 [www.osha.gov/dts/sltc/methods/mdt/mdt1003/1003.html]. Date accessed: October 2015.

## METHOD REVISED BY:

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## **APPENDIX: PREPARATION OF SAMPLING MEDIA**

### **Coating of Silica Gel**

1. Dry 100 g of silica gel (45/60 mesh) at 90 °C for 2 h.
2. Prepare a mercuric cyanide solution in distilled water (2 g mercuric cyanide in 100 mL water).
3. Add the dried silica gel to the mercuric cyanide solution and let set for 15 min with occasional stirring.
4. Drain the excess mercuric cyanide solution and dry the remaining silica gel at 90 °C for 3 h.
5. Cool the silica gel to room temperature in a covered beaker.
6. Expose the silica gel to a humid atmosphere (>80% RH) for 24 h.

### **Preparing the Sampling Tubes**

7. Place a plug of silylated glass wool at the end of a glass tube (6 mm OD and 4 mm ID) about 12 cm long. Pour 300 mg of the treated silica gel into the tube. Place another plug of silylated glass wool behind this front section. Add another 150 mg of the treated silica gel into the tube. Place a final plug of silylated glass wool behind this backup section.
8. Check the pressure drop of a representative sampler. The pressure drop across the tube must be less than 6.7 kPa (50 mmHg) at a flow rate of 0.2 L/min.
9. Flame seal both ends of the sampling tubes.