

PHOSPHINE

6002

PH₃

MW: 34.00

CAS: 7803-51-2

RTECS: SY7525000

METHOD: 6002, Issue 2

EVALUATION: FULL

Issue 1: 15 August 1994

Issue 2: 15 January 1998

OSHA : 0.3 ppm
NIOSH: 0.3 ppm; 1 ppm STEL
ACGIH: 0.3 ppm; 1 ppm STEL
 (1 ppm = 1.39 mg/m³ @ NTP)

PROPERTIES: gas, BP -87.8 °C; vapor density 1.17 (air = 1); spontaneously flammable in air if P₂H₄ is present

SYNONYMS: hydrogen phosphide; phosphorous hydride; phosphorated hydrogen; phosphorous trihydride

APPLICABILITY: The working range is 0.013 to 0.6 ppm (0.02 to 0.9 mg/m³) for a 16-L air sample. The sampler is not commercially available.

INTERFERENCES: The colorimetric determination of phosphate is subject to interference by any species that also forms a molybdate complex under these condition; possible interfering species include PCl₃ and PCl₅ vapors and organic phosphorous compounds.

OTHER METHODS: This revises Method S332 [2]. OSHA Method ID-180, "Phosphine in Workplace Atmospheres", [3] employing potassium hydroxide-impregnated carbon media may be used as an alternative method.

REAGENTS:

1. Potassium dihydrogen phosphate, anhydrous, KH_2PO_4 , ACS reagent grade
2. Sulfuric acid, concentrated, ACS reagent grade
3. Ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$
4. Ferrous ammonium sulfate, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$
5. Potassium permanganate, KMnO_4
6. Stannous chloride, SnCl_2
7. Glycerol
8. Toluene
9. Isobutanol
10. Methanol
11. Water, deionized or distilled.
12. Mercuric cyanide, $\text{Hg}(\text{CN})_2^*$
13. Standard phosphate solution. Dissolve 200 mg KH_2PO_4 in 1 L of distilled water. (1.00 mL = 49.94 μg Pb_5)
14. Molybdate solution. Dissolve 49.4 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and 112 mL concentrated H_2SO_4 in distilled water to a total volume of 1 L.
15. Alcoholic sulfuric acid solution. Add 50 mL of concentrated H_2SO_4 to 950 mL methanol.
16. Toluene-isobutanol solvent. Mix equal volumes of toluene and isobutanol.
17. Ferrous solution. Dissolve 7.9 g $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ and 1 mL concentrated H_2SO_4 in water to a total volume of 100 mL.
18. Stannous chloride solution. Dissolve 0.4 g SnCl_2 in 50 mL glycerol (heat to dissolve).
19. Acidic permanganate solution. Dissolve 0.316 g KMnO_4 and 6 mL concentrated H_2SO_4 in 1 L water.
20. Mercuric cyanide solution. Dissolve 2 g $\text{Hg}(\text{CN})_2$ in 100 mL water.

*See Special Precautions

EQUIPMENT:

1. Sampler: 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 to 0.2 mL/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-, 10-, and 25-mL, and other convenient sizes to make standard dilutions.
8. Volumetric flasks, 10-, 25-, 100-, and 1000-mL.
9. Water bath (maintained at 65-70°C).
10. Graduated cylinders, glass, 10-mL.
11. Syringes, 0.5- and 1.0-mL.
12. Balance.
13. Thermometer.
14. Stopwatch.
15. Barometer.

SPECIAL PRECAUTIONS: Caution should be exercised when preparing the sampling media because mercuric cyanide is toxic. Work only in a hood.

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 and 0.2 L/min for a total sample size of 1 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 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 seconds. Let the separatory funnel stand for 60 seconds 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 to 400 µL of the standard phosphate solution to cover the range 0.1 to 10 µg of P₅H. Add 8 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 seconds. Let the separatory funnel stand for 60 seconds 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 through 18).
 - f. Prepare a calibration graph (absorbance versus µg of P₅H 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 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 through 8) and analyze with working standards (steps 15 through 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 through 18 must be performed within one minute.
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, μg (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 $W_b > W_f/10$, report breakthrough and possible sample loss.
20. Calculate concentration, C , of phosphine in the air volume sampled, V (L).

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was validated over the range 0.195 to 0.877 mg/m^3 at 19 °C and 765.3 mm Hg 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^3 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 $\mu\text{g PH}_3$).

REFERENCES:

- [1] Backup Data Report for Phosphine, S332, prepared under NIOSH Contract No. 210-76-0123, March 17, 1978.
- [2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 5, S332, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
- [3] OSHA Analytical Methods Manual (USDOL/OSHA-SLCAL Method No. ID-80). Publ. No. (ISBN) 0-936712-66-X. American Conference of Governmental Industrial Hygienists, Cincinnati, OH.

METHOD REVISED BY:

Charles Lorberau, NIOSH/DPSE.

APPENDIX: PREPARATION OF SAMPLING MEDIA**Coating of Silica Gel**

1. Dry 100 g of silica gel (45/60 mesh) at 90°C for 2 hours.
2. Prepare a 2% (w/v) mercuric cyanide solution in water (2 g $\text{Hg}(\text{CN})_2$ in 100 mL water).
3. Add the dried silica gel to the mercuric cyanide solution and let set for 15 minutes with occasional stirring.
4. Drain the excess mercuric cyanide solution and dry the remaining silica gel at 90°C for 3 hours.
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 hours.

Preparing the sampling tubes

7. Place a plug of silylated glass wool at the end of a glass tube (6-mm O.D. and 4-mm I.D.) 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 2 inches of mercury at a flow rate of 0.2 L/min.
9. Flame seal both ends of the sampling tubes.