PHOSPHORUS

P_4 MW: 123.90 CAS: 7723-14-0 RTECS: TH3500000

METHOD: 7905, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
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OSHA : 0.1 mg/m^3
NIOSH: 0.1 mg/m^3; Group I Pesticide
ACGIH: 0.1 mg/m^3
(1 ppm = 5.07 mg/m^3 @ NTP)

PROPERTIES: solid; d 1.83 g/mL @ 20 °C; MP 44 °C; BP 280 °C; sublimes; VP 3.5 Pa (2.6 x 10^{-2} mm Hg; 172 mg/m^3) @ 20 °C; oxidizes spontaneously in air

SYNONYMS: white phosphorus; yellow phosphorus.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Tenax GC, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 5 L @ 0.1 mg/m^3
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: 7 days @ 25 °C

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.056 to 0.24 mg/m^3 [1] (12-L samples)

BIAS: + 5.5%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.090 [1]

ACCURACY: ± 21.3%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, PHOSPHORUS FPD

ANALYTE: phosphorus

DESORPTION: 1 mL xylene; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 200 °C
-COLUMN: 80 °C

CARRIER GAS: He, 30 mL/min

COLUMN: 1.8 m x 6-mm OD x 2-mm ID glass; 3% OV-101, 80/100 mesh Chromosorb WHP

CALIBRATION: standard solutions of phosphorus in xylene

RANGE: 0.5 to 5 µg per sample

ESTIMATED LOD: 0.005 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.024 @ 0.6 to 2.4 µg per sample [1]

APPLICABILITY: The working range is 0.04 to 0.8 mg/m^3 (0.0008 to 0.16 ppm) for a 12-L air sample. The method is applicable to vapor-phase phosphorus only. If particulate P_4 is expected in the air sample, use a filter in the sampling train.

INTERFERENCES: None identified.

OTHER METHODS: This combines and replaces S334 [2] and P&CAM 257 [3]. P&CAM 242, utilizing impinger sampler (xylene), has not been revised [4].

REAGENTS:

1. Phosphorus (white), purified, stored under distilled water.*
2. Xylene (mixed), reagent grade.
3. Acetone, purified.
4. Calibration stock solution, 0.20 mg/mL. Prepare under nitrogen or other inert gas. Dissolve a known mass (ca. 2 mg) of acetone-washed, dried white phosphorus in 10 mL xylene. Stir until dissolved. Prepare in duplicate.
5. Helium, prepurified.
6. Hydrogen, prepurified.
7. Air, compressed, filtered.
8. Nitrogen, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: borosilicate glass tube, 7-cm long, 8-mm OD, 6-mm ID, flame-sealed ends with plastic caps, containing two sections of 35/60 mesh Tenax GC (front = 100 mg; back = 50 mg) separated and retained by 2-mm silylated glass wool plugs. Pressure drop across the sampler at 0.2 L/min airflow must be less than 3.3 kPa (25 mm Hg).
   NOTE: If the air sample is expected to contain particulate elemental phosphorus, precede the Tenax tube with a 37-mm diameter, cellulose ester membrane filter.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame photometric detector (phosphorus mode), integrator and column (page 7905-1).
4. Vials, 20-mL, PTFE-lined septum caps.
5. Syringes, 5-, 10- and 25-µL, for making standards and GC injections.
6. Volumetric flasks, 10-mL.
7. Pipet, TD, 1-mL with pipet bulb.
8. Balance, analytical, readable to 0.01 mg.

SPECIAL PRECAUTIONS: White phosphorus may be fatal if ingested, even in small quantities [5]. Phosphorus vapor is toxic; work in a contained atmosphere with adequate care.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal 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 5 to 100 L.
4. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool plugs.
6. Pipet 1.0 mL xylene into each vial. Cap each vial.
   NOTE: Use 5.0 mL xylene for filters, if applicable.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution, or a serial dilution thereof, to xylene in 10-mL volumetric flasks and dilute to the mark to produce phosphorus concentrations in the

range 0.01 to 5 µg/mL.
   b. Analyze with samples and blanks (steps 11 and 12)
   c. Prepare calibration graph (peak area vs. µg phosphorus).

9. Determine desorption efficiency (DE) at least once for each batch of Tenax-GC 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 (2 to 20 µL) of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tub. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. µg phosphorus recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 7905-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the range of the working standards, dilute with xylene, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of phosphorus 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.
14. Calculate concentrations, C, of phosphorus 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:

Method S334 was issued on November 25, 1977 [2], and validated with generated atmospheres using a solution (11 mg/mL) of phosphorus in tetralin in a calibrated syringe drive, verified by independent collection in xylene [1]. Average recovery was 106% with $\hat{S}_r = 7.4\%$ (18 samples) in the range 0.056 to 0.24 mg/m^3 for 12-L samples. In an experiment in which 25-L samples of an atmosphere containing 0.35 mg/m^3 phosphorus vapor were analyzed, the same phosphorus concentration was found in xylene-filled impingers with or without cellulose ester membrane prefilters. Breakthrough (effluent = 5% of test concentration) did not occur after sampling for 240 min at 0.2 L/min from an atmosphere containing 0.311 mg/m^3 at 85% RH. Desorption efficiency for 18 samples in the range 0.6 to 2.4 µg per sample average 95% with $\hat{S}_r = 2.6\%$. The overall precision, $\hat{S}_{rT}$, including pump error was 0.090.

REFERENCES:

[1] Backup Data Report, S334, (November 25, 1977), available as "Ten NIOSH Analytical Methods, Set 5," order No. PB 287-499, from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S334, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] Ibid., Vol. 1, P&CAM 257, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977)
[4] Ibid., P&CAM 242.
[5] Merck Index, 11th ed., Merck & Co., Rahway, NJ (1989).

METHOD REVISED BY:

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