

PHOSPHORUS TRICHLORIDE

6402

PCl₃

MW: 137.33

CAS: 7719-12-2

RTECS: TH3675000

METHOD: 6402, Issue 2

EVALUATION: PARTIAL

Issue 1: 15 May 1985

Issue 2: 15 August 1994

OSHA : 0.5 ppm
NIOSH: 0.2 ppm; STEL 0.5 ppm
ACGIH: 0.2 ppm; STEL 0.5 ppm
 (1 ppm = 5.61 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.574 g/mL @ 21 °C;
 BP 76 °C; MP -112 °C; VP 13 kPa
 (100 mm Hg; 13% v/v) @ 21 °C

SYNONYMS: phosphorous chloride.

SAMPLING		MEASUREMENT	
SAMPLER:	BUBBLER (15 mL H ₂ O)	METHOD:	VISIBLE SPECTROPHOTOMETRY
FLOW RATE:	0.05 to 0.2 L/min	ANALYTE:	molybdenum blue
VOL-MIN:	11 L @ 0.5 ppm	COLOR DEVELOPMENT:	3 mL Br ₂ water + 5 mL Na ₂ MoO ₄ + 2 mL hydrazine sulfate → molybdenum blue
-MAX:	100 L	WAVELENGTH:	830 nm
SHIPMENT:	ship in sealed bubblers	CALIBRATION:	KH ₂ PO ₄ solutions
SAMPLE STABILITY:	unknown	RANGE:	0.03 to 0.5 mg PCl ₃ per sample
FIELD BLANKS:	2 to 10 field blanks per set	ESTIMATED LOD:	3 µg PCl ₃ per sample
ACCURACY		PRECISION (\hat{S}_r):	0.06 @ 0.03 to 0.14 mg PCl ₃ per sample [1]
RANGE STUDIED:	ca. 3.1 mg/m ³ [1]		
BIAS:	not significant [1]		
OVERALL PRECISION (\hat{S}_{rT}):	unknown		
ACCURACY:	not determined		

APPLICABILITY: The working range is 0.2 to 14 ppm (1.2 to 80 mg/m³) for a 25-L air sample.

INTERFERENCES: Phosphorus (V) compounds do not interfere. The sample solutions are stable to oxidation by air during sampling [1].

OTHER METHODS: This revises P&CAM 305 [2].

REAGENTS:

1. Potassium dihydrogen phosphate stock solution, 100 µg H₃PO₄/mL. Dissolve 0.1389 g KH₂PO₄ in distilled H₂O and dilute to 1 L.
2. Calibration stock solution, 10 µg/mL H₃PO₄. Dilute 100 mL KH₂PO₄ stock solution to 1 L with distilled water.
3. Sulfuric acid, 10 N. Slowly add 279 mL conc. H₂SO₄ to 500 mL distilled water. Dilute to 1 L when cool.
4. Sodium molybdate solution. Dilute 25.0 g Na₂MoO₄·2H₂O to 1 L with 10 N sulfuric acid.
5. Bromine water, saturated.* Add sufficient liquid Br₂ to saturate distilled water with stirring.
6. Hydrazine sulfate solution, 1.5 g/L. Dissolve 1.5 g N₂H₆SO₄ in distilled water to make 1 L solution.
7. Hydrazine sulfate, saturated. Add sufficient hydrazine sulfate to distilled water with stirring to saturate.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass midget bubbler* with non-rubber (e.g., PTFE) stopper and fritted glass inlet (Corning EC or 170- to 220-µm max pore); 5-cm glass tube with glass wool plug for protection of pump from splashover.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. Spectrophotometer, reading at 830 nm, with matched glass cuvettes, 1-cm path length.
4. Waterbath, boiling.
5. Pipets, 0.1-, 1-, 2-, 3-, 5- and 25-mL.*
6. Volumetric flasks, 50-mL and 1-L.*
7. Beakers, 50-mL.*
8. Cold water bath.

* Boil all glassware contaminated by phosphate detergent in 1:1 HCl. Rinse thoroughly with distilled water.

SPECIAL PRECAUTIONS: Liquid bromine causes severe eye and skin burns. Bromine vapor is a severe irritant of the eyes and respiratory tract. Permanent breathing difficulty may result [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Add 15 mL distilled water to the bubbler. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for a total sample size of 11 to 100 L.
NOTE: The bubbler must be kept in a vertical position during sampling. If the bubbler solution spills into the trap, discard the sample.
3. Remove the bubbler stem and tap gently against the inside wall of the bubbler to recover as much of the sample solution as possible. Rinse the stem with several mL distilled water, collecting the rinse in the bubbler.
4. Seal the bubbler bottom with a stopper. Alternatively, connect the inlet of the bubbler top to the outlet with PTFE tubing and seal the top to the bottom with tape.

SAMPLE PREPARATION:

5. Transfer contents of the bubbler quantitatively to a 50-mL volumetric flask. Dilute to mark with distilled water and mix.
NOTE: Start reagent blanks at this step.
6. Pipet 25 mL of the diluted sample into a 50-mL beaker.
7. Pipet 3 mL saturated bromine water into the beaker. Let stand 60 sec for oxidation to occur.
NOTE: The purpose of the bromine water is to oxidize PCl₃, present in water as H₃PO₃, to H₃PO₄.

8. Add saturated hydrazine sulfate dropwise until the orange-yellow color of excess bromine is gone; add one drop in excess. Transfer the solution to a second 50-mL volumetric flask. Wash the beaker several times with a few mL of distilled water, adding the wash to the second volumetric flask.
9. Pipet 5 mL sodium molybdate solution and 2 mL of 1.5 g/L hydrazine sulfate solution into the second volumetric flask (containing the oxidized sample). Add identical amounts of reagents to the unoxidized 25-mL sample in the volumetric flask from step 5. Dilute both solutions to the mark with distilled water and shake well.
10. Immerse the volumetric flasks in a boiling water bath for 10 min. Remove and cool rapidly to room temperature in cold water bath. Proceed immediately with the measurement (steps 12 through 14).

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards over the range 3 to 500 $\mu\text{g PCI}_3$ (2 to 360 $\mu\text{g H}_3\text{PO}_4$) per sample.
 - a. Pipet aliquots of calibration stock solution into 50-mL volumetric flasks.
 - b. Prepare (steps 5 through 10) and measure (steps 12 through 14) together with the samples and blanks.
 - c. Construct calibration graph (absorbance vs. μg phosphoric acid).

MEASUREMENT:

12. Set the spectrophotometer according to manufacturer's directions to read at 830 nm.
13. Transfer several mL of the sample or standard solution to a cuvette and place in the spectrophotometer.
14. Record the absorbance reading vs. reagent blank.

CALCULATIONS:

15. Determine from the calibration graph the mass (μg) of phosphoric acid present in each oxidized sample (M_o) and unoxidized sample (M_u) and the average media blank (M_b).
16. Calculate the concentration (C) of PCI_3 in the air volume sampled, V (L):

$$C = \frac{(2 \cdot M_o - 2 \cdot M_u - M_b) \cdot 1.4}{V}, \text{ mg/m}^3.$$

where: 1.4 = M.W. PCI_3 /M.W. H_3PO_4 = 137.3/98.0.

EVALUATION OF METHOD:

This method is based on P&CAM 305 [1,2]. In that work, recoveries were determined for samples spiked at 0.5, 1, and 2 times the OSHA standard to be 0.992, 1.04, and 1.05. The overall precision and accuracy have not been completely determined. In one experiment, the efficiency of bubbler collection of PCI_3 was found to be 0.99 ± 0.06 based on six pairs of bubblers sampling from a 3.1 mg/m^3 atmosphere generated using a diffusion cell. At the concentrations studied, PCI_3 tended to react with water vapor in the air to produce fogs of H_3PO_3 . Attempts to separate the H_3PO_3 aerosol from PCI_3 vapor by means of polyvinyl chloride membrane filters were unsuccessful because of reaction between the filters and PCI_3 . The reactions for the molybdenum blue color development are:

- (1) $\text{PCI}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3 + 3\text{HCl}$
- (2) $\text{H}_3\text{PO}_3 + \text{Br}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + 2\text{HBr}$
- (3) $\text{H}_3\text{PO}_4 + \text{Na}_2\text{MoO}_4 + \text{N}_2\text{H}_6\text{SO}_4 \rightarrow \text{molybdenum blue}$

REFERENCES:

- [1] Arthur D. Little, Inc. Development of Methods for the Determination of Phosphoric Acid, PCl_3 , PCl_5 and P_4S_{10} in Air, Final Report of NIOSH Contract 210-76-0038 (unpublished, May 10, 1977).
- [2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, P&CAM 305, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
- [3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

Martin Abell, NIOSH/DPSE; P&CAM 305 originally developed under NIOSH Contract 210-75-0038.