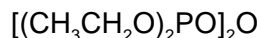


TETRAETHYL PYROPHOSPHATE

2504



MW: 290.19

CAS: 107-49-3

RTECS: UX6825000

METHOD: 2504, Issue 2

EVALUATION: FULL

Issue 1: 15 February 1984

Issue 2: 15 August 1994

OSHA : 0.05 mg/m³ (skin)
NIOSH: 0.05 mg/m³ (skin); Group I Pesticide
ACGIH: 0.05 mg/m³ (skin)
 (1 ppm = 11.86 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.185 g/mL @ 20 °C;
 BP 124 °C @ 1 mm Hg; MP 32 °C;
 VP 0.063 kPa (0.00047 mm Hg; 0.62 ppm)
 @ 30 °C

SYNONYMS: diphosphoric acid tetraethyl ester; pyrophosphoric acid tetraethyl ester; TEPP

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (2 Chromosorb 102 tubes in series, 100 mg and 50 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, FPD
FLOW RATE:	0.01 to 0.2 L/min	ANALYTE:	TEPP
VOL-MIN:	20 L @ 0.05 mg/m ³	DESORPTION:	1 mL toluene; stand 60 min
-MAX:	48 L	INJECTION	
SHIPMENT:	routine	VOLUME:	5 µL
SAMPLE		TEMPERATURE-INJECTION:	200 °C
STABILITY:	at least 8 days @ 25 °C [1]	-DETECTOR:	200 °C
BLANKS:	2 to 10 field blanks per set	-COLUMN:	115 °C
ACCURACY		CARRIER GAS:	N ₂ or He, 30 mL/min
RANGE STUDIED:	0.025 to 0.102 mg/m ³ [1] (48-L samples)	COLUMN:	2 m x 2-mm ID glass; Super-Pak 20M
BIAS:	- 0.6%	CALIBRATION:	TEPP in toluene
OVERALL PRECISION ($\hat{S}_{r,T}$):	0.086 [1]	RANGE:	1 to 6 µg per sample [1]
ACCURACY:	± 17.4%	ESTIMATED LOD:	0.1 µg per sample [1]
		PRECISION (\hat{S}_r):	0.039 [1]

APPLICABILITY: The working range is 0.025 to 0.15 mg/m³ for a 40-L air sample. The method is useful for both area and personal samples.

INTERFERENCES: None identified.

OTHER METHODS: This is P&CAM 336 [2] in a revised format.

REAGENTS:

1. TEPP, purified*.
NOTE: TEPP is hygroscopic and easily hydrolyzed.
2. Tripropyl phosphate, reagent grade, or other suitable internal standard.
3. Toluene, reagent grade.
4. Eluent: Dilute a weighed amount of tripropyl phosphate to 100 mL with toluene. Concentration of solution must be within the linear range of the FPD.
5. Nitrogen or helium, purified.
6. Hydrogen, prepurified.
7. Air, filtered.
8. Calibration stock solution, 1.18 mg/mL. Dilute 11.8 mg (10 μ L) TEPP to 10 mL with eluent. Prepare in duplicate.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two glass tubes, 10-cm long, 8-mm OD, 6-mm ID, flame-sealed ends, front tube containing a 100-mg section of extracted resin and a back containing a 50-mg section, retained by silylated glass wool plugs in each tube. Pressure drop across the tubes in series at 1 L/min airflow must be less than 3.4 kPa. (Tubes commercially available as SKC, Inc. ST 226-105).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame photometric detector, phosphorus filter, integrator and column (page 2504-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringe, volumetric, 10- and 100- μ L.
6. Flasks, volumetric, 10-mL.
7. Pipettes, volumetric, 1-mL, with pipet bulb.
8. File.

SPECIAL PRECAUTIONS: TEPP is a cholinesterase inhibitor and can be absorbed through the skin. Wear protective gloves and suitable protective clothing when handling the pure material [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Connect the two sorbent tubes with a short piece of flexible tubing. 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 20 to 48 L.
4. Separate the front and backup tubes. Cap the tubes with plastic (not rubber) caps. This prevents migration of TEPP between sorbent sections. 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. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 60 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.1 to 6 μ g TEPP per sample.
 - a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
 - b. Analyze together with samples and blanks (steps 11 and 12).
 - c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. μ g TEPP).

9. Determine desorption efficiency (DE) at least once for each batch of Chromosorb 102 used for sampling in the calibration range (step 8). 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 of calibration stock solution directly onto front sorbent section with a microliter syringe.
 - c. Cap the tube. 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 TEPP recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure 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 2504-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of TEPP 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 concentration, C, of TEPP 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 P&CAM 336 [2] was evaluated over the range 0.025 to 0.102 mg/m^3 at 21.5 °C and 735.3 mm Hg using 48-L samples [1,4]. Overall precision, \hat{S}_{rT} , was 0.086 with an average recovery of 99.4%, representing a non-significant bias. The concentration of TEPP was independently verified by sampling the generator with toluene-filled bubblers and analysis by GC/FPD. Desorption efficiency averaged 0.994 in the range 1.1 μg to 4.8 μg per sample. After sampling an atmosphere containing 0.41 $\mu\text{g/m}^3$ at 0.18 L/min at 90% RH for 300 min, only 0.2% of the influent concentration was detected breaking through the sorbent bed.

REFERENCES:

- [1] Backup Data Report S305, TEPP, prepared under NIOSH Contract No. 210-76-0123 (August, 1979).
- [2] NIOSH Manual of Analytical Methods, 2nd ed., V. 6, P&CAM 336, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
- [3] Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).

- [4] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Eugene R. Kennedy, Ph.D., NIOSH/DPSE; P&CAM 336 originally developed under NIOSH Contract No. 210-76-0123.