$C_{14}H_{14}NO_4PS$ W: 323.31 CAS: 2104-64-5 RTECS: TB1925000

METHOD: 5012, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
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OSHA : 0.5 mg/m^3 (skin)
NIOSH: 0.5 mg/m^3 (skin); Group I Pesticide
ACGIH: 0.5 mg/m^3 (skin)

PROPERTIES: solid; MP 36 °C; d 1.268 g/mL @ 25 °C
VP 0.04 Pa (0.0003 mm Hg, 5 mg/m^3) @ 100 °C

SYNONYMS: phenylphosphonothioic acid O-ethyl-O,p-nitrophenyl ester

SAMPLING

SAMPLER: FILTER (glass fiber)

FLOW RATE: 1 to 2 L/min

VOL-MIN: 15 L @ 0.5 mg/m^3
-MAX: 700 L

FIELD TREATMENT: transfer filters within 1 h of sampling to vial

SHIPMENT: in vials

SAMPLE STABILITY: at least 7 days @ 25 °C

ACCURACY

RANGE STUDIED: 0.3 to 1.2 mg/m^3 [1] (120-L samples)

BIAS: 0%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.06 [1,2]

ACCURACY: ± 11.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FLAME PHOTOMETRIC

ANALYTE: EPN

DESORPTION: 15 mL isooctane

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 215 °C
-DETECTOR: 215 °C
-COLUMN: 205 °C

CARRIER GAS: N_2 or He, 60 mL/min

COLUMN: 2 m x 6-mm glass, packed with 3% OV-1 on 100/120 mesh Gas Chrom Q

CALIBRATION: solutions of the EPN in isooctane

RANGE: 6 to 170 µg per sample

ESTIMATED LOD: 2 ng per sample [1]

PRECISION ($\bar{S}_r$): 0.04 [1]

APPLICABILITY: The working range is 0.05 to 1.5 mg/m^3 EPN for 120-L air samples. Malathion and Parathion have also been determined by this procedure.

INTERFERENCES: None known.

OTHER METHODS: This method replaces Method S285 [2]. The method of Hill and Arnold [3] has also been used for analysis of pesticides. Method 5600 is an alternative method for organophosphorus pesticides.

REAGENTS:

1. EPN.*
2. Isooctane, chromatoquality.*
3. Calibration stock solution, 15 mg/mL isoctane (prepare fresh daily):
   NOTE: 4 µL of this solution contains a mass of EPN (0.06 mg) equivalent to a 120-L air sample at OSHA PEL.
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Oxygen, purified.
7. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass fiber filter (Gelman Type AE or equivalent), 37-mm, in a two-piece polystyrene cassette supported by a backup pad.
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
3. Gas chromatograph, column bypass valve, flame photometric detector, phosphorus filter, integrator and column (page 5012-1).
4. Vials, 20-mL, glass with PTFE-lined caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.
7. Pipets, 15-mL, with pipet bulb.
8. Tweezers.

SPECIAL PRECAUTIONS: EPN is a highly toxic cholinesterase inhibitor with cumulative effects [4,5]. Special care must be taken to avoid inhalation or skin contact.

Isooctane is flammable. Prepare all samples in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate in the range 1 to 2 L/min for a total volume of 15 to 700 L. Do not exceed 2 mg total dust loading on the filter.
3. Within 1 h after sampling, transfer the glass fiber filter with tweezers to a clean 20-mL vial.

SAMPLE PREPARATION:

4. Pipet 15 mL isooctane into each vial. Cap each vial and swirl the contents for 1 h.

CALIBRATION AND QUALITY CONTROL:

5. Prepare at least six working standards covering the analytical range of the method, by diluting aliquots of the calibration stock solutions to 15 mL with isooctane.
   a. Analyze calibration standards in triplicate with the unknowns, blanks and other quality control spiked samples following steps 7 through 9.
   b. Prepare calibration graph (peak area or peak height vs. µg of EPN).
6. Analyze recovery (R) samples with each sample set, in duplicate.
   a. Place filter media blanks in clean 20-mL vials.
   b. Inject analyte calibration stock solution directly onto the filter with a microliter syringe.
   c. Cap the vial and allow to stand overnight.
   d. Analyze according to steps 4 and 7 through 9.
   e. Calculate recovery (µg found on filter divided by µg added to filter).

MEASUREMENT:

7. Set gas chromatograph to conditions given on page 5012-1, optimizing the air, hydrogen and oxygen according to the GC manufacturer's instructions.
8. Inject 5-µL sample aliquots using solvent flush technique.
   a. Vent the solvent peak by opening the column bypass valve at the time of injection. Close the column bypass valve after the solvent peak has eluted (ca. 30 sec) and before the

analyte peak elutes.

b. Make replicate injections of samples and standards.

9. Measure peak area or peak height.

CALCULATIONS:

10. Read the mass, µg per sample, of EPN found on the sample filters, W, and average media blank filters, B, from the calibration graph.
11. Calculate the concentration, C, of EPN in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S285 for EPN was issued on April 26, 1976 [2]. The precision and bias were obtained by generating atmospheres of EPN at one-half, one and two times the OSHA standards [1,6]. Test atmospheres were generated using Trion-6 EPN (Wilbur Ellis Co.). Gelman Type AE glass fiber filters were used for all sampling and measurement recovery studies. Collection efficiency of the glass fiber filter was determined to be 1.0 and losses from vaporization of known amounts of EPN deposited on a glass fiber filter were negligible [4]. Filters spiked with solutions of EPN gave quantitative recoveries after storage for 7 days at 25 °C.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S285, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S285, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[3] Hill, Robert H., Jr. and James E. Arnold. A Personal Air Sampler for Pesticides, Arch. Environ. Contam. Toxicol., 8, 621-628 (1979).

[4] Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).

[5] NIOSH/OSHA Occupational Safety and 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, D.C. 20402.

[6] 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:

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