$(C_2H_5O)_2P(=S)O(CH_2)_2SC_2H_5$ (1) MW: 258.34 CAS: 8065-48-3 RTECS: TF3150000
$(C_2H_5O)_2P(=O)S(CH_2)_2SC_2H_5$ (2)

METHOD: 5514, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 0.1 mg/m^3 (skin)
NIOSH: 0.1 mg/m^3; Group I Pesticide
ACGIH: 0.01 ppm (0.11 mg/m^3) (skin)
(1 ppm = 10.56 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.18 g/mL @ 20 °C;
BP 134 °C @ 270 kPa; MP -25 °C;
VP 0.1 kPa (0.001 mm Hg; 1 ppm)
@ 33 °C

SYNONYMS: phosphorothioic acid O,O-diethyl O-[2-(ethylthio)ethyl]ester (Demeton O)mixture with O,O-diethyl S-[2-(ethylthio)ethyl]phosphorothioate (Demeton S); Systox; Bayer 8169; Demox; mercaptophos

SAMPLING

SAMPLER: FILTER + SORBENT TUBE (2-µm mixed cellulose ester + XAD-2, 150 mg/75 mg)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 30 L
-MAX: 500 L

SHIPMENT: transfer filter and front sorbent section to same vial

SAMPLE STABILITY: at least 7 days @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.03 to 0.19 mg/m^3 [1] (480-L samples)

BIAS: 0.49%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.03 [1]

ACCURACY: ± 13.9%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, PHOSPHORUS FPD

ANALYTE: (1) Demeton O and (2) Demeton S

DESORPTION: 5 mL toluene, 15 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 210 °C
-COLUMN: 165 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: glass, 1.2 m x 3-mm OD; 1.5% OV-17/1.95% OV-210 on 100/120 mesh Chromosorb WHP

CALIBRATION: solutions of Demeton in toluene

RANGE: 3 to 100 µg per sample

ESTIMATED LOD: 0.1 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.03 [1]

APPLICABILITY: The working range is 0.015 to 10 mg/m^3 for a 200-L air sample. The use of a capillary column, e.g., a DB-210, may improve sensitivity and resolution.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S280 [2].

REAGENTS:

1. Demeton O/Demeton S mixture of known concentration, reagent grade.*
2. Toluene, reagent grade.
3. Methanol, reagent grade.
4. Methylene chloride, reagent grade.
5. Calibration stock solution, ca. 2.4 mg/mL Demeton O and 8.3 mg/mL Demeton S. Dilute 100 µL of commercially available mixture to 10 mL with toluene.
6. Hydrogen, prepurified.
7. Nitrogen, purified.
8. Oxygen, purified.
9. Air, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter, supported by a stainless steel screen in a polystyrene cassette filter holder followed by a tube, 7 cm long, 8-mm OD, 6-mm ID, packed with two sections (front = 150 mg; back = 75 mg) of 20/50 mesh XAD-2. Two plastic plugs are required for capping the tube after sampling. Tubes are commercially available. (SKC, Inc. 226-30-05, or equivalent).
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Vial, scintillation, with PTFE-lined cap, graduated at 15 mL.
4. Gas chromatograph with phosphorus-sensitive FPD, integrator, and column (page 5514-1).
5. Syringes, 5-, 10- and 25-µL, for making standard solutions and GC injections.
6. Volumetric flasks, 10-mL.
7. Pipets, 5-mL.
8. Tweezers.

SPECIAL PRECAUTIONS: Demeton is a cholinesterase inhibitor and readily absorbed through the skin; baseline and routine red blood cell cholinesterase monitoring is recommended [3,4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of tubes immediately before sampling. Attach filter cassette to inlet of XAD-2 tube with short piece of tubing. Connect the outlet of sampler to pump.
3. Sample at an accurately known flow rate between 0.2 and 1 L/min for a total sample size of 30 to 500 L.
4. Transfer the filter, the front glass wool plug, and the front sorbent section to the same vial. Cap the tube containing the back sorbent section.
5. Pack the samples securely for shipment.

SAMPLE PREPARATION:

6. Place the back sorbent section of the XAD-2 tube in a separate vial. Discard the remaining glass wool plugs.
7. Add 5.0 mL toluene to each vial. Cap each vial.
8. Allow to stand 15 min with occasional agitation. Analyze within one day.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range 0.1 to 100 µg Demeton per sample for each isomer.
   a. Add known amounts of calibration stock solution to toluene in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 12 and 13).
   c. Prepare calibration graph (peak area vs. µg of each isomer).
10. Determine desorption efficiency (DE) at least once for each lot of XAD-2 used for sampling in the calibration range (step 9). 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 (1 to 20 µL) of calibration stock solution, or a serial dilution thereof, 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 together with working standards (steps 12 and 13).
   e. Prepare a graph of DE vs. µg of each Demeton isomer recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5514-1. Inject sample aliquot manually using solvent flush technique or with autosampler. t_r = 4 min for Demeton O and 7.5 min for Demeton S under these conditions.
   NOTE: If peak area is above the linear range of the working standards, dilute with toluene, reanalyze, and apply the appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, µg (corrected for DE) of Demeton (sum of Demeton O and Demeton S) found on the sample filter plus front sorbent section ($W + W_f$), back (W_b) sorbent section, and on the average media blank filter (B) and front (B_f) and back (B_b) media blank sorbent sections.
15. Calculate concentration, C, of Demeton in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Method S280 for Demeton was issued on August 3, 1979 [2], and validated in the range 0.03 to 0.19 mg/m^3 for 480-L samples [1,5]. The substance used to generate test atmospheres at 25 °C and 760 mm Hg in dry air was a 0.075% solution of Demeton (21% Demeton O, 74.5% Demeton S) in toluene [1,5]. The atmosphere was generated by the aspirator method. Collection efficiencies and recovery were 1.00 for the isomers in the range 5 to 270 mg per sample. Sample filters extracted in toluene immediately and stored one week at ambient conditions gave recoveries of 100%. Overall precision for sampling plus measurement, $\hat{S}_{rT}$, was 0.08. No significant bias was found for either substance. No breakthrough was observed after 12 hours of sampling at 1 L/min in atmospheres containing 0.14 mg/m^3 Demeton O and 0.17 mg/m^3 Demeton S at 80% RH.

REFERENCES:

[1] Backup Data Report, S280 (NIOSH, unpublished, August 3, 1979).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6, S280, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[3] NIOSH 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/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.
[5] 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:

Gangadhar Choudhary, Ph.D., CDC/ATSDR; S280 originally validated under NIOSH Contract 210-76-0123.