$((CH_3)_2NC(=S)S-)_2$ MW: 240.43 CAS: 137-26-8 RTECS: JO1400000

METHOD: 5005, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 5 mg/m^3
NIOSH: 5 mg/m^3; Group I Pesticide
ACGIH: 1 mg/m^3

PROPERTIES: white crystalline powder; d 1.29 g/mL; MP 155 °C; VP not significant

SYNONYMS: bis(dimethylthiocarbamoyl)disulfide; tetramethylthiuram disulfide; tetramethylthioperoxydicarbonic diamide

SAMPLING

SAMPLER: FILTER (1-µm PTFE membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 10 L
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: 7 days at 25 °C

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: desirable; 1 to 5g

ACCURACY

RANGE STUDIED: 3 to 12 mg/m^3 [1] (240-L samples)

BIAS: - 0.18%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.055 [1]

ACCURACY: ± 10.67%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: Thiram

EXTRACTION: (filter) 10 mL CH_3CN, 30 min; (cassette top) 10 mL CH_3CN rinse

INJECTION VOLUME: 5 µL

MOBILE PHASE: 60% acetonitrile/40% water, 1 mL/min

COLUMN: µ-Bondapak C_{18} (30 cm x 3.9-mm-ID stainless steel); ambient temperature

DETECTOR: UV @ 254 nm, 1-cm cell

CALIBRATION: standard solutions of Thiram in acetonitrile

RANGE: 0.1 to 3 mg per sample [1]

ESTIMATED LOD: 0.005 mg per sample [1]

PRECISION ($\hat{S}_r$): 0.012 [1]

APPLICABILITY: The working range is 0.5 to 15 mg/m^3 for a 200-L air sample. NIOSH researchers have used this method at facilities that use Thiram as an insecticide.

INTERFERENCES: None known.

OTHER METHODS: This is Method S256 [2] in a revised format. An earlier spectrophotometric method, P&CAM 228 [3], has not been revised because of excessive analytical variability [4].

REAGENTS:

1. Acetonitrile, HPLC grade.*
2. Water, distilled, deionized.
3. Thiram, reagent grade.*
4. Air or nitrogen, compressed, for drying syringes.
5. Calibration stock solution, 0.75 mg/mL. Dissolve an accurately weighed 7.5 mg Thiram in acetonitrile and dilute to 10 mL. Prepare fresh daily in duplicate.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 1-µm PTFE membrane filter (Millipore FA or equivalent), 37-mm diameter, two-piece polystyrene cassette filter holder with backup pad, sealed with tape or a shrinkable band. Filter holders made of Tenite should not be used.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Liquid chromatograph, UV detector at 254 nm,integrator and column (page 5005-1).
4. 13 mm x 5 µm PTFE filters and stainless steel filter holder to protect the LC column.
5. Vials, 20-mL, glass, PTFE-lined screw caps.
6. Syringe, 1-mL, with Luer-Lok fitting.
7. Pipets, 10-mL, with pipet bulb.
8. Tweezers.
9. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Acetonitrile is toxic and flammable; work with it only in a hood.

Thiram is an irritant of skin and mucous membranes, a skin sensitizer, and suspected teratogen [5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1 to 4 L/min for a total sample size of 10 to 400 L. Do not exceed 2 mg total dust loading on the filter.
3. Collect a bulk sample (1 to 5 g) in a glass vial with PTFE-lined cap; ship separately from filters.

SAMPLE PREPARATION:

4. Remove filter from cassette with tweezers and place in 20-mL vial.
5. Add 10 mL acetonitrile. Cap the vial.
6. Rinse the inside top of cassette with 10 mL acetonitrile into a 20-mL vial. Cap the vial.
7. Agitate samples during the 30-min desorption period.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.005 to 3 mg Thiram per sample.
   a. Add known amounts of calibration stock solution to acetonitrile in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 9 and 10).
   c. Prepare calibration graph (peak area vs. mg Thiram).

MEASUREMENT:

9. Set liquid chromatograph to conditions on page 5005-1. Inject 10-µL sample aliquot. Rinse and dry syringe between injections.
10. Measure peak area.

CALCULATIONS:

11. Read the mass, mg, of Thiram found in the sample filter (W_f) and top rinse (W_t) and in the average media blank (B) from calibration graph.
12. Calculate the concentration of Thiram, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_f + W_t - B) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S256 was issued on June 8, 1979 [2], and validated by collecting 18 samples (six each at one-half, one and two times the OSHA standard) from dynamically-generated test atmospheres using Thiram 65 (65% Thiram; Mayer Chemical Co.), as well as a set of six samples which was stored at room temperature for seven days to establish stability [1,4]. The stored sample results were within 2.1% of samples analyzed after one day, indicating adequate storage stability for seven days. Eighteen more samples were spiked directly (six each at one-half, one and two times the OSHA standard). The pooled relative standard deviation for these three sets of samples was found to be 0.012. The average recovery for all three levels was 99.8%; therefore, there is no bias for this method. The pooled relative standard deviation for the three sets of samples collected from test atmospheres was 0.022. Test atmospheres at 12 mg/m^3 Thiram were sampled with PTFE filters followed by bubblers containing acetonitrile; no detectable Thiram (LOD = 0.005 mg) was found in the bubblers indicating that vapor pressure of Thiram was insignificant.

REFERENCES:

[1] Backup Data Report S256, NIOSH Contract 210-76-0123, available as Order No. PB 81-244634 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 5, S256, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] Ibid, V. 1, P&CAM 228, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[4] Failure Report S256, NIOSH Contract CDC-99-74-45 (unpublished, 1976).
[5] Criteria for a Recommended Standard...Occupational Exposure During Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).
[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:

Yvonne T. Gagnon, NIOSH/DPSE; S256 originally validated under NIOSH Contract 210-76-0123.