THIRAM 5005

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

METHOD: 5005, Issue 3 **EVALUATION:** FULL **Issue 1:** 15 February 1984 **Issue 3:** 15 March 2016

OSHA: 5 mg/m³
NIOSH: 5 mg/m³; Group I Pesticide

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 SAMPLES: desirable; 1 to 5g

ACCURACY

RANGE STUDIED: 3 to 12 mg/m³ [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: C18 (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 ($\bar{S}_r$): 0.012 [1]

APPLICABILITY: The working range is 0.5 to 15 mg/m³ 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 polytetrafluoroethylene (PTFE) membrane filter, 37-mm diameter, two-piece polystyrene cassette filter holder with backup pad, sealed with tape or a shrinkable band.
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 lock style 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):

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

EVALUATION OF METHOD:

Method S256 was issued on June 8, 1979 [2], and validated by collecting 18 samples (six each at 0.5, 1 and 2 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 0.5, 1 and 2 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] Stanford Research Institute [1979]. Backup Data Report: Method S256. Menlo Park, CA: Stanford Research Institute. NIOSH contract 210-76-0123. Available as order no. PB-81-244634 from NTIS.

[2] NIOSH [1979]. Thiram in air: Method S256. In: Taylor DG, ed. NIOSH manual of analytical methods. 2nd. ed. (Vol 5). Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) 79-141.

[3] NIOSH [1976]. Thiram in air: Method P&CAM 228. In: Taylor DG, ed. NIOSH manual of analytical methods. 2nd ed. (Vol 1). Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-157-A.

[4] IIT Research Institute [1976]. Failure Report: Method S256. Chicago, IL: IIT Research Institute. NIOSH contract no. 99-74-45. Unpublished.

[5] NIOSH [1978] NIOSH criteria for a recommended standard: occupational exposure during manufacture and formulation of pesticides, Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 78-174.

[6] NIOSH [1980]. NIOSH research report – development and validation of methods for sampling and analysis of workplace toxic substances. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 80-133.

METHOD REVISED BY:

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

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