



# THIRAM

5005



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/m<sup>3</sup>  
**NIOSH:** 5 mg/m<sup>3</sup>; 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		MEASUREMENT	
<b>SAMPLER:</b>	FILTER (1- $\mu\text{m}$ PTFE membrane)	<b>TECHNIQUE:</b>	HPLC, UV DETECTION
<b>FLOW RATE:</b>	1 to 4 L/min	<b>ANALYTE:</b>	Thiram
<b>VOL-MIN:</b>	10 L	<b>EXTRACTION:</b>	(filter) 10 mL CH <sub>3</sub> CN, 30 min; (cassette top) 10 mL CH <sub>3</sub> CN rinse
<b>-MAX:</b>	400 L	<b>INJECTION VOLUME:</b>	5 $\mu\text{L}$
<b>SHIPMENT:</b>	routine	<b>MOBILE PHASE:</b>	60% acetonitrile/40% water, 1 mL/min
<b>SAMPLE STABILITY:</b>	7 days at 25 °C	<b>COLUMN:</b>	C18 (30 cm x 3.9-mm-ID stainless steel); ambient temperature
<b>BLANKS:</b>	2 to 10 field blanks per set	<b>DETECTOR:</b>	UV @ 254 nm, 1-cm cell
<b>BULK SAMPLES:</b>	desirable; 1 to 5g	<b>CALIBRATION:</b>	standard solutions of Thiram in acetonitrile
<b>ACCURACY</b>		<b>RANGE:</b>	0.1 to 3 mg per sample [1]
<b>RANGE STUDIED:</b>	3 to 12 mg/m <sup>3</sup> [1] (240-L samples)	<b>ESTIMATED LOD:</b>	0.005 mg per sample [1]
<b>BIAS:</b>	-0.18%	<b>PRECISION (<math>\bar{S}_r</math>):</b>	0.012 [1]
<b>OVERALL PRECISION (<math>\hat{S}_{r-T}</math>):</b>	0.055 [1]		
<b>ACCURACY:</b>	$\pm 10.67\%$		

**APPLICABILITY:** The working range is 0.5 to 15 mg/m<sup>3</sup> 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- $\mu$ m 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  $\mu$ m 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.

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**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].

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**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- $\mu$ L 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,  $C$  ( $\text{mg}/\text{m}^3$ ), in the air volume sampled,  $V$  (L):

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

**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  $\text{mg}/\text{m}^3$  Thiram were sampled with PTFE filters followed by bubblers containing acetonitrile; no detectable Thiram ( $\text{LOD} = 0.005 \text{ mg}$ ) 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. 2<sup>nd</sup> 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:**

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