

CAPTAN AND THIOPHANATE-METHYL in Handrinse

9202

Thiophanate-Methyl: $C_{12}H_{14}N_4O_4S_2$ MW: 342.40 CAS: 23564-05-8 RTECS: BA3675000
 Captan: $C_9H_8Cl_3NO_2S$ 300.59 133-06-2 GW 5075000

METHOD: 9202, Issue 1

EVALUATION: PARTIAL

Issue 1: 15 March 2003

Captan Thiophanate-methyl
OSHA: N/A N/A
NIOSH: N/A N/A
ACGIH: N/A N/A

PROPERTIES:

Thiophanate-methyl: Colorless prisms, mp 181.5-182.5°C, soluble in acetone, methanol, chloroform, acetonitrile, insoluble in water.
Captan: Odorless crystals, mp 178°C, soluble in chloroform, practically insoluble in H₂O.

NAMES & SYNONYMS:

Thiophanate-Methyl: Topsin-M; [1,2-phenylenebis(iminocarbonothioyl)]bisdimethyl ester carbamic acid
Captan: N-(trichloromethyl)thio-4-cyclohexene-1,2-dicarboximide; Captec

SAMPLING	MEASUREMENT
<p>SAMPLER: POLYETHYLENE BAG 12" x 18", polyethylene bag containing 150 mL isopropanol</p> <p>SHIPMENT: transfer wash to 250-mL wide-mouth glass jars with PTFE-lined caps. Ship cold.</p> <p>SAMPLE STABILITY: at least 28 days at 4° C</p> <p>BLANKS: 2 to 10 field blanks per set</p>	<p>TECHNIQUE: HPLC, UV detector</p> <p>ANALYTE: Captan and Thiophanate-methyl</p> <p>INJECTION VOLUME: 5 µL</p> <p>MOBILE PHASE: A=2% n-propanol in water, 0.02 M TEA- PO₄ adjusted to pH 7.0 +/- 0.1 using phosphoric acid; B=2% n-propanol in acetonitrile. Gradient increasing from 20% B to 70% B over 20 min., decreasing to 20% B (2 min.) hold at 20% B (5 min.)</p> <p>COLUMN: Reversed Phase C-18, 4µ, 250 x 2.00 mm (or equivalent).</p> <p>DETECTOR: UV @ 200 nm</p> <p>CALIBRATION: Solutions prepared in isopropanol</p> <p>RANGE: Table 1</p> <p>ESTIMATED LOD: Table 1</p> <p>PRECISION (S_r): Table 1</p>
ACCURACY	
<p>RANGE STUDIED: Not studied</p> <p>BIAS: Not determined</p> <p>OVERALL PRECISION (S_{r,t}): Not determined</p> <p>ACCURACY: Not determined</p>	

APPLICABILITY: This method was developed for the analysis of captan and thiophanate-methyl in an isopropanol hand rinse solution from orchard workers. In addition, this method may also be used to analyze other fungicides and pesticides that may be present in the field as long as they are sufficiently separated from the analytes by the analytical conditions of the method and soluble in isopropanol. (Figure 1.) Outside of the investigation into possible analytical interferences, extensive research was not completed on other pesticides and fungicides.

INTERFERENCES: The potential interferences include other organic compounds, in particular other agricultural chemicals that have the same retention time on a C18 column. Confirmation of the target fungicide can be checked by using an amino or phenyl LC column. Possible interferences include: ziram, myclobutanil, mancozeb, imidacloprid, and phosmet.

OTHER METHODS: This method was developed in conjunction with NMAM 5606, Thiophanate-methyl in air and NMAM 9205, Captan and Thiophanate-methyl on dermal patches.

REAGENTS:

1. Isopropanol, HPLC pesticide grade.*
2. Acetonitrile, HPLC grade.*
3. Triethylamine (TEA).*
4. Deionized water.
5. Thiophanate-methyl* stock solution, 10 mg/mL. Prepare in acetonitrile.
6. Captan* stock solution, 5 mg/mL. Prepare in acetonitrile.
7. TEA-PO₄ Preservative. Dissolve 1.4 mL of TEA in 90 mL of deionized water in a 100 mL volumetric flask. Add phosphoric acid to lower pH to 7.0 +/- 0.1 as indicated by a calibrated pH meter. Bring volume to 100 mL with water. Keep tightly capped and refrigerated. Solution stable for 12 months.
8. Mobile phase A. Combine 20 mL of n-propanol and 2.8 mL triethylamine in a 1 L volumetric flask and bring to volume using deionized water. Adjust pH to 7.0 (+/- 0.1) with phosphoric acid using a pH meter. Final concentrations: 2% n-propanol, 0.02 M TEA-PO₄. Degas prior to use.
9. Mobile phase B. Transfer 20 mL of n-propanol to a 1 L volumetric flask and adjust to volume with acetonitrile. Degas prior to use.
10. Ortho-phosphoric acid* >85% by weight, ACS grade or better.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: 8" x 12" Scienceware™ Reusable Heavyweight Polyethylene Bags, 4 mm wall thickness (Bel-Art No. H13178-0812).
2. Container: 250 mL screw-top container with PTFE liner.
3. High Performance Liquid Chromatograph (HPLC) with UV detector.
4. Autosampler or injection valve capable of 5 µL injections.
5. Analytical column: Phenomenex® Synergi™ 4µ Hydro-RP 80A (250 x 2.00 mm) or equivalent.
6. Vials, 2-mL with PTFE-lined caps.
7. Syringes, 50-µL, 1-mL, and 5-mL.
8. Volumetric flasks, 5-mL, 100-mL, and 1-L.
9. PTFE syringe filter, 4-mm, 0.45-µm pore.
10. pH meter.
11. Graduated cylinders, 50-mL.
12. Pipettes, glass, disposable, 2-mL.
13. Bagged refrigerant.

SPECIAL PRECAUTIONS: Thiophanate-methyl: Avoid inhaling vapors or dust; avoid skin contact. Wear gloves and suitable clothing when handling pure material. Solvents: Avoid skin contact and open flame. Use in a hood. Phosphoric acid: Avoid skin contact. Captan: Use in hood. Avoid contact with skin, eyes, and clothing and ingestion or inhalation. Eye protection should be worn.

SAMPLING:

1. Pour 150 mL of isopropanol into the polyethylene bag.
2. Insert hand into bag. Wrap the top of the bag securely around the forearm, several inches above the wrist.
NOTE: Allergies to alcohol are extremely rare. Before conducting the handwash, check to see if the person has ever had a reaction to alcohols, or is taking medications that could react with the alcohol. Some skin conditions, such as cuts, abrasions, and eczema can be irritated by contact with alcohols. If the person's hand seems "dried-out" after the handwash, hand lotion can be applied.
3. Shake hand in alcohol with constant back and forth motion for 30 seconds. Remove hand from bag and dry with paper towel.
4. Transfer solution to glass jar, cap securely.
5. Label and pack for shipment.
6. For field blank, add 150 mL isopropanol to a clean bag, shake for 30 seconds, then transfer the solvent to a glass jar for shipment.

SAMPLE PREPARATION:

7. Prepare analyst spike samples, solutions of isopropanol spiked with varying concentrations of the analytes of interest used for quality assurance, when field samples are received and store them together. Analyze with the field samples, blanks, and the liquid standards. Include unused 150 mL isopropanol wash of a polyethylene sampling bag as a media blank.
8. Remove a 1 mL aliquot from the sample container and filter with a 4mm 0.45 µm syringe filter.

CALIBRATION AND QUALITY CONTROL:

9. Determine retention times for analytes using the column and chromatographic conditions as shown on pages 9202-1 & 9202-2. The approximate retention time of thiophanate-methyl is 11 minutes and captan is 19 minutes. (See Figure 1.)
10. Calibrate daily with at least six working standards containing each of the two analytes and covering the analytical range for thiophanate-methyl and captan.

MEASUREMENT:

11. Set LC conditions according to manufacturer's recommendations. Set the wavelength for detection at 200 nm and the flow rate at 0.200 mL/min.
12. Inject a 5 µL sample aliquot with autosampler.
NOTE: If the peak area of a sample is greater than the area of the highest standard, dilute with isopropanol and reanalyze.
13. Measure peak area of the analyte.

CALCULATIONS:

14. Perform a separate regression analysis of peak area vs. concentration of standard for each of the analytes. Determine the concentration, C (µg/mL), of the analyte in each sample from the calibration graph.
15. Calculate the mass of each analyte, M (µg), in the submitted sample volume, V(mL). Use a volume of 150 mL for the volume of the sample.

$$M = C \cdot V, \mu\text{g / sample}$$

EVALUATION OF METHOD:

This method was evaluated with a recovery study at room temperature over the range of 8949-60270 µg/sample for thiophanate-methyl and 13140-44070 µg/sample for captan using spiked laboratory samples with respective average recoveries in the range of 91.1-100% and 93.7-95.3%. [1] A recovery study at 4°C was also performed over the range of 8940-60420 µg/sample for thiophanate-methyl and 13130-43930 µg/sample for captan using spiked laboratory samples with respective average recoveries in the range of 101-111% and 102-105%. The storage study at room temperature was completed at 33990 µg/sample for thiophanate-methyl and 26200 µg/sample for captan with respective recovery averages of 102-107% and 102-127% over the 28 days of the study. The storage study at 4°C was completed at 34130 µg/sample for thiophanate-methyl, and 25520 µg/sample for captan with respective recovery averages of 110-121% and 102-112% over the 27 days of the study.

Originally, carbendazim was included in the investigation since it is a breakdown product of thiophanate-methyl. Attempts to quantitatively measure carbendazim suffered from reproducibility problems prompting carbendazim's removal from this method as an analyte that can be quantified. This method may be used to qualitatively determine carbendazim. Under method conditions, its approximate retention time is 6 minutes.

REFERENCES:

- [1] Andrews RN, Jaycox LB [2002]. Back-up Data Report for captan and thiophanate-methyl in handrinse, Cincinnati, OH: National Institute for Occupational Safety and Health, unpublished.
- [2] NIOSH [1998]. Method 5601. In: Cassinelli ME, O'Connor PF, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed, 2nd supplement. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publ 98-119.

AUTHORS:

Ronnee N. Andrews, NIOSH/ DART
Larry B. Jaycox, Ph.D., NIOSH/ DART

Table 1.

Analyte	Range ($\mu\text{g}/\text{sample}$)	Estimated LOD ($\mu\text{g}/\text{sample}$)	Precision ($\%$)
Captan	410 - 44070	123	0.0326
Thiophanate-methyl	198 - 60270	60	0.0181

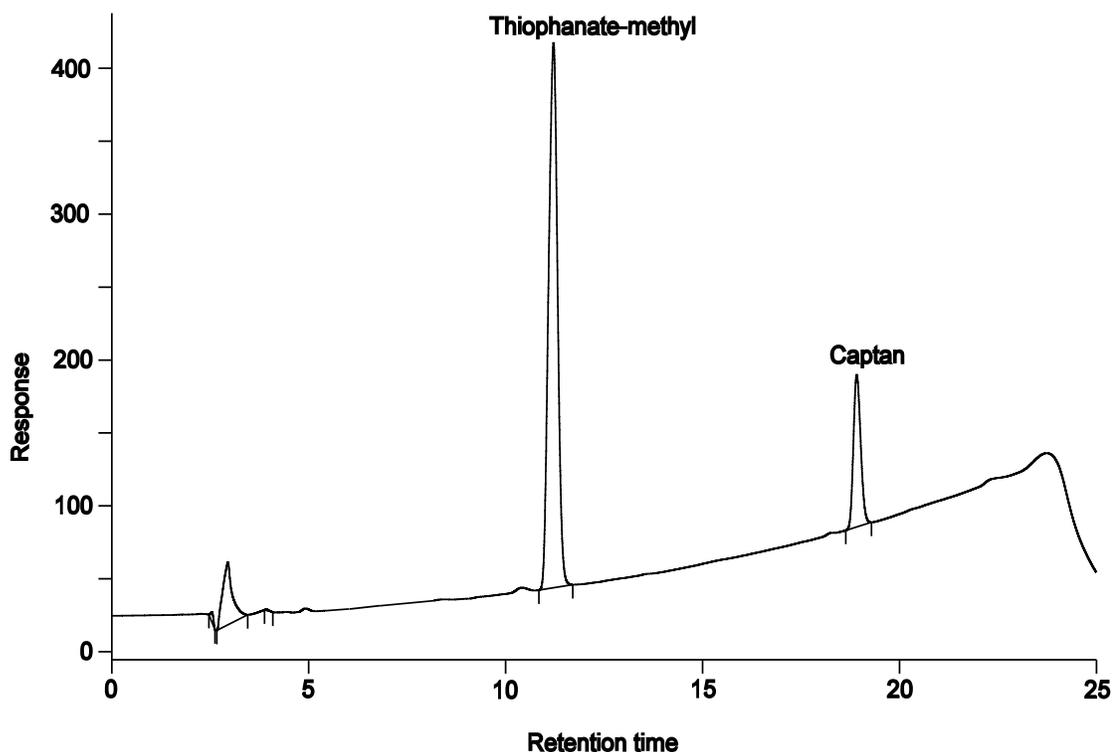


Figure 1. A typical chromatogram from the analysis of a hand rinse storage sample. The concentrations of the analytes shown here are: thiophanate-methyl - 226 $\mu\text{g}/\text{mL}$ and captan - 175 $\mu\text{g}/\text{mL}$.