

California Department of Food and Agriculture
Center for Analytical Chemistry
Environmental Monitoring Section
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Title: Determination of 1,3-dichloropropene (Telone) and Methyl Isothiocyanate (MITC) Absorbed on Charcoal

1. Scope:

This section method (SM) provides stepwise procedure for 1,3-dichloropropene (Telone) and Methyl Isothiocyanate (MITC) analysis in SKC charcoal tubes and is followed by all authorized EMON personnel.

2. Principle:

Telone and MITC are desorbed from the SKC charcoal tubes with 0.1% CS₂ in methylene chloride and analyzed by a gas chromatogram with a mass selective detector (MSD) operated in the selective ion monitoring mode (SIM).

3. Safety:

- 3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.
- 3.2 Methylene chloride is a regulated and controlled carcinogenic hazardous substance. It must be stored and handled in accordance with California Code of Regulations, Title 8, Subchapter 7, Group 16, Article 110, Section 5202.

4. Interferences:

There were no matrix interferences that caused quantitative problems during method development and validation.

5. Apparatus and Equipment:

- 5.1 Vortex-vibrating mixer
- 5.2 Gas Chromatograph equipped with a mass selective detector (MSD)

6. Reagents and Supplies:

- 6.1 1,3-dichloropropene (cis & trans) CAS#542-75-6
- 6.2 Methyl Isothiocyanate CAS#556-61-6
- 6.3 Methyl Chloride, nanograde or equivalent pesticide grade

- 6.4 Carbon disulfide, nanograde or equivalent pesticide grade
- 6.5 Coconut charcoal sorbent tubes, SKC Inc., 863 Valley View Rd. 84 PA.15330, Cat # 226-09
- 6.6 Test tube
- 6.7 Disposable Pasteur pipettes
- 6.8 ORBO tube cutter, Supelco #2-0596
- 6.9 File or dremel for scoring tubes
- 6.10 Acrodisc disposable nylon filters, 0.45 μ m
- 6.11 Recommended analytical column:

Restek Rtx-200 trifluoropropylmethyl polysiloxane, 60 m x 0.32 mm id x 1.5 μ m film thickness.

7. Standards Preparation:

- 7.1 Obtain individual Telone and MITC stock standards of 1.0 mg/mL from the CDFA/CAC Standards Repository. Dilute the standards to 10 μ g/mL with methylene chloride for identification purposes. Obtain a combination 10 mg/mL from CDFA/CAC Standards Repository in acetone for preparation of standards used for fortification.

Use the individual stock standards to prepare a combination standard in methylene chloride, which can be diluted to prepare the working standards used for instrument calibration. The working standards shall range from 0.025 μ g/mL to 2 μ g/mL in concentration.

- 7.2 Keep all standards in the designated refrigerator for storage.

- 7.3 The expiration date of each standard is six months from the preparation date.

8. Sample Preservation and Storage:

All samples waiting for extraction shall be stored in a freezer (-10 \pm 10 $^{\circ}$ C).

9. Test Sample Preparation:

- 9.1 Background Preparation

The Department of Pesticide Regulation (DPR) provides the

coconut charcoal sorbent tubes for background to be used in method development and QC.

9.2 Spike

9.2.1 Break tips of a SKC tube with the tube cutter.

9.2.2 Spike a client requested amount of Telone and MITC into the charcoal tube and let it stand for 1 minute. Follow the test sample extraction procedure.

9.3 Test Sample Extraction

9.3.1 Remove samples from freezer and allow samples to come to room temperature before starting extraction.

9.3.2 Fold a sheet of paper into quarters, reopen and place under the tube to catch any charcoal spills.

9.3.3 Pipet 5 mL of 0.1% CS₂ in methylene chloride into labeled test tube.

9.3.4 Remove caps from charcoal tube and score tube with a file or dremel just above the wire spring. Snap the tube; remove the wire spring and glass wool plug with forceps. Transfer the wire spring and glass wool plug to the tube containing 5 mL of 0.1% CS₂ in methylene chloride.

9.3.5 Place the large open end of the sample tube into the mouth of the test tube insert a 9" disposable pipette from the opposite end to push remaining glass wool plug and charcoal out of tube into test tube. Cap the test tube immediately.

9.3.6 Vortex and then allow sample to sit and desorb for 30 minutes with occasionally vortexing in between.

9.3.7 Filter the sample through a 0.45 µm Nylon Acrodisc and collect it in an autosampler vial.

10. Instrument Calibration:

- 10.1 The calibration standard curve consists of a minimum of three levels. The concentrations of 0.025, 0.1, 0.25, 0.5, 1.0 and or 2 $\eta\text{g}/\mu\text{L}$ standards are recommended.
- 10.2 The calibration curve is obtained using linear regression with a correlation coefficient (r) equal to or greater than 0.995.

11. Analysis:

11.1 Injection Scheme

The instrument may need to be conditioned with a matrix blank or old sample before running the following sequence of Standard Curve, Solvent, Matrix Blank, Matrix Spike, Test Samples (maximum of 10 – 12) and Standard Curve.

11.2 GC Instrumentation

11.2.1 Analyze Telone and MITC by a gas chromatograph equipped with a mass selective detector.

11.2.2 Recommended instrument parameters: Injector 210 °C; msd transfer line heater 280 °C; initial oven temperature 40 °C, hold 4 min., ramp at 12 °C/min. to final temperature of 160 °C and then ramp at 40 °C/min to 240 °C; for a final time 1 min.; injection volume 2 μL .

Ions Selected for SIM Acquisition:

Cis Dichloropropene	75 , 110, Ret. time 10.65 min.
Trans Dichloropene	75 , 110, Ret. time 11.39 min.
MITC	72 , 73 , Ret. time 12.01 min.

Quantitative ions are in **bold**.
Dwell time 30 milliseconds

12. Quality Control:

12.1 Method Detection Limits (MDL)

Method Detection Limit (MDL) refers to the lowest concentration of the analyte that a method can detect reliably. To determine the MDL, 7 charcoal tubes are spiked with a combination standard of Telone and MITC and processed through the entire method along with a blank. The standard deviation derived from the spiked sample recoveries was used to calculate the MDL for each analyte using the following equation:

$$\text{MDL} = tS$$

Where t is the Student t test value for the 99% confidence level with $n-1$ degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the $n=7$ replicates used to determine the MDL, $t=3.143$.

The results for the standard deviations and MDL are in Appendix 1.

12.2 Reporting Limit (RL)

Reporting limit (RL) refers to a level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. The RL is chosen in a range 1-5 times the MDL, as per client agreement. The reporting limit for Telone and MITC is 0.1 μg per sample.

12.3 Method Validation

The method validation consisted of five sample sets. Each set included three levels of fortification and a method blank. All spikes and method blanks were processed through the entire analytical method. Spike levels and recoveries for the Telone and MITC are shown in Appendix 2.

12.4 Control Charts and Limits

Control charts were generated using the data from the method validation for each analyte. The upper and lower warning and control limits are set at ± 2 and 3 standard deviations of the % recovery, respectively, shown in Appendix 2.

12.5 Acceptance Criteria

12.5.1 Bracketing standard curves should have a percent change $\leq 20\%$. The % change in response was calculated as follows:

$$\% \text{ change in response} = \frac{\text{Absolute value of response (std before - std after)}}{\text{Std before}} \times 100$$

12.5.2 Each set of samples will have a matrix blank and a spiked matrix sample.

12.5.3 The retention time should be within ± 2 per cent of that of the standards.

12.5.4 The recoveries of the matrix spikes shall be within the control limits.

12.5.5 The sample shall be diluted if results fall outside of the calibration curve. For Telone if the total peak height for cis and trans is greater than that of the highest standard, dilute the sample and reinject.

13. Calculations:

Telone was expressed as the sum of its isomers. Therefore, the total residue should be calculated using the sum of its peaks responses.

Quantitation is based on an external standard (ESTD) calculation using either the peak area or height. The software uses a linear curve fit, with all levels weighted equally. Alternatively, at the chemist's discretion, concentrations may be calculated using the response factor for the standard whose value is $< 30\%$ to the level in the sample. In the case of Telone, results were calculated using the average response factor for the curve since the cis and trans isomers responses were added together.

$$\mu\text{g/sample} = (\text{sample peak area or ht}) \times (\text{final volume of sample}) / (\text{response factor})$$

where:

$$\text{Response Factor} = [\sum(\text{std peak ht}_n / \text{std conc.}_n) / n]$$

14. Reporting Procedure:

Sample results are reported out according to the client's analytical laboratory specification sheets.

15. Discussion and References:

15.1 Telone and MITC were analyzed on two different detectors in previous methods. This method was developed so that both compounds could be analyzed using the MSD.

15.2 It was found that 0.1% CS₂ needed to be added to the extraction solvent to achieve acceptable recoveries for MITC. Ethyl acetate was used previously for extraction of MITC with 0.1% CS₂ added, but the ethyl acetate had interferences that effected cis 1,3 - dichloropropene. Different brands and grades of ethyl acetate were tried to see if the interference could be avoided, but were not successful. Methylene chloride had no interfering peaks and with the 0.1% CS₂ added gave acceptable recoveries for Telone and MITC.

15.5 References:

15.51 Mok, Tina *MITC in Air Samples BY GC/NPD*, EM 41.9, 1999, California Department of Food and Agriculture Center for Analytical Chemistry, Environmental Monitoring Laboratory, 3292 Meadowview Road, Sacramento, California 95832

15.52 Standard Operating Procedure Sampling and Analysis of 1,3-dichloropropene (Telone) and Methyl Isothiocyanate (MITC) in Application and Ambient Air using Gas Chromatography/Mass Selsctive Detector, California Environmental Protection Agency Air Resources Board, 06/25/01 version

15.53 Lew, Robert, *Determination of Telone (1,3-dichloropropene) Absorbed on Charcoal*, EM 59.5 1995, California Department of Food and Agriculture Center for Analytical Chemistry, Environmental Monitoring Laboratory, 3292 Meadowview Road, Sacramento, California 95832

Appendix 1

The determination of Method Detection Limit (MDL) and Reporting Limit (RL)

	Telone	MITC
Spike Level	0.15 µg/sample	0.15 µg/sample
blk	N/D	N/D
spk1	0.134	0.130
spk2	0.150	0.142
spk3	0.144	0.137
spk4	0.134	0.130
spk5	0.141	0.135
spk6	0.135	0.126
spk7	0.148	0.144
SD	0.007	0.007
MDL (µg/sample)	0.0208	0.0206
RL (µg/sample)	0.1	0.1

Appendix 2

Method Validation Data and Control Limits							
Analyte	Spike Level ppt	Recovery %					
		Set 1	Set2	Set 3	Set 4	Set 5	
Telone	2	2.08	2.23	2.13	2.28	2.20	SD = 6.27
	20	20.2	21.1	22.6	23.8	22.6	Mean = 109
	200	201	229	197	231	214	UCL 128 LCL 90.1
MITC	2	1.90	2.07	1.97	2.10	2.02	SD = 6.46
	20	18.7	19.6	21.1	22.1	20.9	Mean = 97.6
	200	185	214	185	216	198	UCL 117 LCL 78.2

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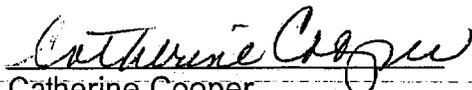
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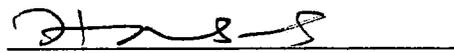
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