Determination of 1,3-dichloropropene (Telone) absorbed on charcoal

1. **Scope**:

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

2. **Principle**:

Telone is desorbed from the SKC charcoal tubes with methylene chloride and analyzed by a gas chromatogram with a mass selective detector (MSD).

3. **Safety**:

3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.

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 Methylene Chloride, nanograde or equivalent pesticide grade
6.3 Anasorb charcoal sorbent tubes, SKC Inc., 863 Valley View Rd. 84 PA.15330, Cat # 226-09
6.4 Test tube
6.5 Disposable Pasteur pipettes
6.6 File or dremel for scoring tubes
6.7 Acrodisc disposable nylon filters, 0.45µm

6.8 Recommended analytical column:

Agilent CP-Select 624 CB, 60 m x 0.32 mm id x 1.8 µm film thickness.

7. Standards Preparation:

7.1 Obtain individual Telone stock standards of 10 mg/mL from the CDFA/CAC Standards Repository.

Use the individual stock standards to prepare the working standards used for instrument calibration. The working standards shall range from 0.01 µg/mL to 5.0 µg/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 °C).

9. **Test Sample Preparation**:

9.1 Spike

9.1.1 Break tips of a SKC tube with the tube cutter.
9.1.2 Spike a client requested amount of Telone into the charcoal tube and let it stand for 1 minute. Follow the test sample extraction procedure.

9.2 Test Sample Extraction

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

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

9.2.3 Pipet 10 mL of 0.1% CS2/methylene chloride into labeled test tube.

9.2.4 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 charcoal to the tube containing 10 mL of methylene chloride.

9.2.5 If extracting the bottom section as a separate sample, place the large open end of the sample tube into the mouth of a test tube insert a 9" disposable pipette from the opposite end to push remaining glass wool plug and charcoal out of Anasorb tube into a second labeled test tube. If extracting the bottom section along with the top section, push the glass wool plug and charcoal into the same test tube with the front section. Cap the test tube immediately.

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

9.2.7 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 0.01, 0.05, 0.10, 0.5, 1.0, 2.5 and 5 µg/mL 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 and Standard Curve.

11.2 GC Instrumentation

11.2.1 Analyze Telone by a gas chromatography equipped with an MSD detector.

11.2.2 Recommended instrument parameters: Injector 220 °C; MSD transfer line heater 220 °C; initial oven temperature 40 °C, hold 3 min., ramp at 15 °C/min. to temperature of 180 °C, hold for 1.0 min. then ramp at 60 °C/min to 260 °C; for a final time 1 min.; injection volume 2 µL.

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:

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 three sample sets. Each set included eight levels of fortification and a method blank. All spikes and method blanks were processed through the entire analytical method. Spike levels and recoveries for Telone 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 ≤ 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:**

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.

µg/sample= (sample peak area or ht) x (final volume of sample) /(response factor)

where:
Response Factor = [Σ(std peak ht_nstd $conc._n$/n

14. Reporting Procedure:

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

15. Discussion and References:

15.1 References:

15.1.1 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

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

15.1.3 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

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

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

Appendix 2

Set 1	cis-1,3-D	trans-1,3-D
Conc Spiked (µg)	Percent Recovery (%)	Percent Recovery (%)
0.1	111	95.7
0.5	92.8	93.2
2.5	96.4	96.8
5.0	97.0	97
10.0	98.5	98.6

Set 2	cis-1,3-D	trans-1,3-D
Conc Spiked (µg)	Percent Recovery (%)	Percent Recovery (%)
0.1	91.6	80.4
0.5	91.6	92.0
2.5	94.4	94.8
5.0	94.4	94.8
10.0	94.9	94.4

Set 3	cis-1,3-D	trans-1,3-D
Conc Spiked (µg)	Percent Recovery (%)	Percent Recovery (%)
0.1	89.4	81.4
0.5	86.0	85.6
2.5	91.2	90.8
5.0	92.4	91.4
10.0	98.0	97.4

Set 4	cis-1,3-D	trans-1,3-D
Conc Spiked (µg)	Percent Recovery (%)	Percent Recovery (%)
0.1	41.9	75.1
0.5	78.2	85.6
2.5	92.4	92.0
5.0	90.8	89.6
10.0	92.0	90.8

Set 5	cis-1,3-D	trans-1,3-D
Conc Spiked (µg)	Percent Recovery (%)	Percent Recovery (%)
0.1	96.2	78.5
0.5	89.2	90.0
2.5	94.0	94.0
5.0	90.6	90.2
10.0	99.6	99.5

	cis-1,3-D	trans-1,3-D
Average	91.4	90.8
SD	11.8	6.43
UCL	127	110
uwl	115	104
lwl	67.8	77.9
LCL	56.0	71.5

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11/14/20	Added in new validation results