Appendix I. Chemical Analytical Method
1,3-dichloropropene - sorbent tubes
California Department of Health Services Laboratory

State of California
Air Resources Board
Monitoring and Laboratory Division/ELB

Standard Operating Procedure for the Analysis of
Telone (1,3-dichloropropene) in Ambient Air
(Revised with breakthrough data Sept. 8, 1994)
(Revised with additional stability data January 18, 1996)

1. SCOPE

This is a gas chromatography/electron capture method for the determination of 1,3-
dichloropropene from ambient air samples. The method was adapted from NIOSH Method
1003 (Issued) 2/14/84).

2. SUMMARY OF METHOD

The exposed charcoal tubes are stored in an ice chest or refrigerator until desorbed with 3
ml of carbon disulfide. The injection volume is 2 ul. A gas chromatograph with an
electron capture detector is used for analysis.

3. INTERFERENCES/LIMITATIONS

Method interferences may be caused by contaminants in solvents, reagents, glassware
and other processing apparatus that can lead to discrete artifacts or elevated baselines. A
method blank must be done with each batch of samples to detect any possible method
interferences.

4. EQUIPMENT AND CONDITIONS

A. INSTRUMENTATION:
    Varian 3400 gas chromatograph
    Varian 604 Data System

    Detector: 350°C
    Injector: 250°C
    Column: J&W Scientific DB-624, 30 meter, 0.32 mm i.d., 1.0 um film
              thickness.

    Program: Initial 40°C, hold 1 min.; to 70°C @ 50 C/min., hold 1 min.; to 82°C @
    1°C/min., hold 0.0 min.; to 225°C @ 50°C/min., hold 5 min. End = 22.46 min. $t_R$cis
    = 10.4 min., $t_R$trans - 12.2 min.

    Splitter open @ 0.8 min.

    Flows:
    column: He, 1.7 ml/min, 8 psi.
    splitter: 37 ml/min.

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B. AUXILIARY APPARATUS:
1. Glass amber vials, 4 ml capacity with septum caps.
2. Vial Shaker, SKC, or equiv.

C. REAGENTS
1. Carbon Disulfide, ACS Grade, or better
2. Telone (cis-1,3-dichloropropene and trans-1,3-dichloropropene mixture), Chem Service PS-152, 99+%, or equiv.

5. ANALYSIS OF SAMPLES

1. It is necessary to analyze a solvent blank with each batch of samples. The blank must be free of interferences. A solvent blank must be analyzed after any sample which results in possible carry-over contamination.

2. At least one calibration sample must be analyzed for each batch of ten samples. The response of the standard must be within 10% of previous calibration analyses.

3. Carefully score the primary section end of the sampled charcoal tube above the retainer spring and break the score. Remove the glass wool plug from the primary end of the charcoal tube with forceps and place it into a 4 ml amber colored sample vial. Pour the charcoal into the vial and carefully add 3.0 ml carbon disulfide. CAUTION: HEAT WILL BE GENERATED. Seal the vial.

Retain the secondary section of the charcoal tube for later analysis to check the possibility of breakthrough.

4. Place the sample vial on a desorption vibrator for 45 minutes. Remove the carbon disulfide extract and store in a second vial at 4°C until analysis.

5. After calibration of the GC system, inject 2.0 ul of the extract. If the resultant peaks for telone have a measured area greater than that of the highest standard injected, dilute the sample and re-inject.

6. Calculate the concentration in ug/ml based on the data system calibration response factors. If the sample has been diluted, multiply the calculated concentration by the dilution factor.

7. The atmospheric concentration is calculated according to:

Conc., ug/m^3 = (Extract Conc., ug/ml X 3 ml) / Air Volume Sampled, m^3

6. QUALITY ASSURANCE

A. Instrument Reproducibility

Triplicate injections of 3 standards at three different concentrations were made to establish the reproducibility of this instrument. This data in Table 1.

TABLE 1. INSTRUMENT REPRODUCIBILITY

AMOUNT INJECTED (ug/ml)		INTEGRETATION COUNTS			
trans	cis	trans	(%)	cis	(%)
0.024	0.076	15,099 ± 209	(±1%)	10,808 ± 178	(±2%)
0.24	0.76	141,742 ± 3,675	(±3%)	96,384 ± 1,939	(±2%)
2.4	7.6	1,716,441 ± 28,757	(±2%)	1,372,607 ± 41,371	(±3%)

B. Linearity

A five point calibration curve was made ranging from 0.05 ug/ml to 10.0 ug/ml. The corresponding equation and correlation coefficient is:

total (cis + trans) $y = 3.173 \times 10^{-6}X + 0.0650$ Corr. = .9991

The standard deviation of these values based on triplicate injections was <3% for each concentration.

C. Minimum Detection Limit

Using the equation above and the data below, the minimum detection limit for Telone was calculated by:

$$MDL = |I| + 3(s.d._{low})$$

where: $|I|$ = the absolute value of the intercept of the standard curve (from above).

$s.d._{low}$ = the standard deviation of the lowest concentration used for the standard curve.

lowest concentration used = 0.05 + 0.001 ug/ml

$MDL = |0.0650| + 3(0.001) = 0.068$ ug/ml

Using 3 ml extraction volume and an average of 4.3 m^3 sample volume:

$$\frac{0.068\ ug/ml \times 3\ ml}{4.3\ m^3} = 0.05\ ug/m^3$$

Because of the high sensitivity, a MDL of 0.1 ug/m^3 is recommended to insure reliability of the data.

D. Collection and Extraction Efficiency (Recovery)

Collection and extraction efficiency data for Telone on charcoal is presented in TABLE 2. Note that no breakthrough occurred at the levels tested.

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TABLE 2. COLLECTION AND EXTRACTION EFFICIENCY FOR TELONE ON CHARCOAL

CIS			TRANS			TOTAL		
* Amount Spiked (ug)	Amount Recovered (ug)	(%)	Amount Spiked (ug)	Amount Recovered (ug)	(%)	Amount Spiked (ug)	Amount Recovered (ug)	(%)
0.76	0.63 ± 0.07	(83)	0.24	0.27 ± 0.02	(113)	1.0	0.90 ± 0.08	(90)
7.6	7.8 ± 0.3	(103)	2.2	2.0 ± 0.1	(83)	10.0	9.8 ± 0.3	(98)
15.2	14.8 ± 2.2	(97)	4.8	4.4 ± 0.8	(92)	20.0	19.2 ± 3.0	(96)
30.4	25.5 ± 0.7	(84)	9.6	8.8 ± 0.2	(92)	40.0	34.3 ± 0.9	(86)

* Amount spiked on to primary section of charcoal tube. The tube was then subjected to an air flow of approximately 3 lpm for 24 hours. The primary and secondary sections were then desorbed with 3.0 ml carbon disulfide and analyzed by capillary column GC/ECD. No Telone was found in the secondary charcoal section.

E.   Storage Stability

Storage stability studies were done in triplicate for 1.0 ug telone spikes on charcoal tube primary sections over a period of 38 days. The percent recovery data for storage stability is presented in TABLE 3.

TABLE 3. TELONE STORAGE STABILITY AT 4°C

AMOUNT SPIKED (cis + trans)	PERCENT RECOVERY				
	1 Day	3 Days	5 Days	11 Days	38 Days
1.0 ug	93 ± 8	71 ± 11	72 ± 5	76 ± 5	66 ± 4

Additional stability studies were conducted as part of the quality assurance program during a lengthy Telone monitoring program in Kern County during 1995. The results are included on the next page.

In-house Stability Study 10-11/95			
Day	Level (ug)	Recovered	Percent
0 (neat)	1.5	1.7	113
2	1.5	1.4	93
14	1.5	1.2	80
14	7.5	8.8	117
14	15.0	16.0	107
22	1.5	1.2	80
22	7.5	8.1	108
22	15.0	16.0	107
34	1.5	0.90	60

F. Breakthrough

The secondary section of two high level field samples were analyzed for
breakthrough. The primary sections contained 588 ug and 727 ug of Telone. No
Telone was detected in either secondary section.

METHOD RESOLUTION REQUEST

METHOD NO: Telone-ARB recommended method adopted from NIOSH Method 1003(issued 2/14/84).

VERSION DATE Revised 1/18/96

SECTION NO: 4.A.
Method uses DB-624 column.

PROBLEM: There is no known problem with this column. This column would have to be replaced for the analysis of the other analytes in this study. Changing columns require down-time and other unexpected delays before the instrument is stabalized.

SUGGESTED RESOLUTION: DB-5 is used for chloropicrin. Since the telone isomers are well resolved on DB-5 it would be more expedient to use DB-5 for both analytes.

Mario Fracchia   *signature*   10/5/99
                 EHLB Analyst   Date

APPROVED RESOLUTION _____   _____
                          DPR Representative   Date

DPR Discussion:

Telone1.doc

METHOD RESOLUTION REQUEST

METHOD NO: Telone-ARB recommended method adopted from NIOSH Method 1003(issued 2/14/84).

VERSION DATE_Revised 1/18/96

SECTION NO: 4.A.
Method uses DB-624 column.

PROBLEM: We are using DB-5, 30 meter, 0.25mm i.d., 1.0um thickness. Accordingly, the GC conditions were altered for maximum performance.

SUGGESTED RESOLUTION: Temperature programming conditions are slightly different. They are: 40°C for 2 minutes, 10°C / min, to 250°C, no hold time. Splitter on at 0.7 min. Splitter flow=100cc/min.

Mario Fracchia   _(signature)_   10/6/99
                     EHLB Analyst   Date

APPROVED RESOLUTION _____   _____
                           DPR Representative   Date

DPR Discussion:

Telone2.doc

METHOD RESOLUTION REQUEST

METHOD NO: Telone-ARB recommended method adopted from NIOSH Method 1003(issued 2/14/84).

VERSION DATE Revised 1/18/96

SECTION NO. 5.3

PROBLEM: Using 100% CS2 as the desorbant contaminates the ECD and requires many hours for the detector to recover.

SUGGESTED RESOLUTION: Use 10% CS2 in hexane as the desorbant. No poisoning of the detector was observed at this level.

Mario Fracchia   *Mario Fracchia*   10/6/99
                     EHLB Analyst   Date

APPROVED RESOLUTION _____   _____
                         DPR Representative   Date

DPR Discussion:

Telone3.doc

METHOD RESOLUTION REQUEST

METHOD NO: Telone-ARB recommended method adopted from NIOSH Method 1003(issued 2/14/84).

VERSION DATE Revised 1/18/96

SECTION NO. 5.2

PROBLEM: A minimum of one calibration standard employed as a quality control sample, is utilized in each sample analysis batch. The sample analysis acceptance criteria for the entire batch is determined by the calibration standard quality control sample.

SUGGESTED RESOLUTION: The full range of calibration standards are analyzed with each batch analysis, inter-dispersed with the samples. Typical standards are as follows: 15, 30, 63, 125, 250, 500, 1000, 2000, 4000 ng/mL. Quantitation is achieved employing the calibration curve generated with each sample batch.

Mario Fracchia   *signature*   10/5/99
                        EHLB Analyst   Date

APPROVED RESOLUTION _____   _____
                                DPR Representative   Date

DPR Discussion:

Telone4.doc

METHOD RESOLUTION REQUEST

METHOD NO: Telon-ARB recommended method adopted from NIOSH Method 1003(issued 2/14/84).

VERSION DATE Revised 1/18/96

SECTION NO. 5.3

PROBLEM: Desorbant is added to the charcoal, consequently the charcoal is not initially covered by the desorbant. Because of an exothermic reaction between the desorbant and the charcoal, there exists the potential for volatile loss of the analyte adsorbed on the charcoal.

SUGGESTED RESOLUTION: The desorbant is first added to the extraction vial and then the charcoal is added. In this way, the potential for volatile loss is minimized by the heat capacity of the desorbant.

Mario Fracchia   *Mario Fracchia*   10/5/99
                        EHLB Analyst   Date

APPROVED RESOLUTION _____   _____
                              DPR Representative   Date

DPR Discussion:

Telone5.doc

METHOD RESOLUTION REQUEST

METHOD NO: Telon-ARB recommended method adopted from NIOSH Method 1003(issued 2/14/84).

VERSION DATE Revised 1/18/96

SECTION NO. 5.4

PROBLEM: Extraction time is specified as 45 minutes for CS_2. EHLB is using a 10% CS_2 in hexane extraction solvent, which is less polar, in order to avoid poisoning the detector.

SUGGESTED RESOLUTION: To ensure maximum extraction efficiency, the extraction time was increased to 4 hours. This precaution was employed based on general laboratory practice, in order to maximize recoveries at low analyte levels for the less polar desorbant.

Mario Fracchia   _(signature)_   10/5/99

                 EHLB Analyst   Date

APPROVED RESOLUTION _____   _____

                     DPR Representative   Date

DPR Discussion:

Telone6.doc

METHOD RESOLUTION REQUEST

METHOD NO:Telon-ARB recommended method adopted from NIOSH Method 1003(issued 2/14/84).

VERSION DATE Revised 1/18/96

SECTION NO. 5.3

PROBLEM: No internal standard is proposed. Greater precision can be accomplished with an internal standard.

SUGGESTED RESOLUTION: Bromoform is used as the internal standard, which is added after desorption of the charcoal with 10% CS_2 in hexane. The vial containing the bromoform, desorbant, and charcoal is quickly mixed, followed immediately by the transfer of the extract to an auto sampler vial.

Mario Fracchia   *Mario Fracchia*   10/6/99
                   EHLB Analyst   Date

APPROVED RESOLUTION _____   _____
                        DPR Representative   Date

DPR Discussion:

Telone7.doc

METHOD RESOLUTION REQUEST

METHOD NO: Telone-ARB recommended method adopted from NIOSH Method 1003(issued 2/14/84).

VERSION DATE Revised 1/18/96

SECTION NO. 6.B

PROBLEM: Method calls for a 5-point calibration curve. Only one standard is included per batch as a quality control sample. The number of replicates is not specified.

SUGGESTED RESOLUTION : EHLB generates a 10-point calibration curve utilizing duplicate injections. See method resolution Telon4 for specific levels.

Mario Fracchia   *Mario Fracchia*   10/6/99
                         EHLB Analyst   Date

APPROVED RESOLUTION _____   _____
                              DPR Representative   Date

DPR Discussion:

Telone.8doc