Determination of Bromomethane, cis-1,3-Dichloropropene and trans-1,3-Dichloropropene in Air Samples Collected in Summa Canisters

1. Scope:

This Section Method (SM) is for the analysis of the selected compounds collected in summa canisters. The canisters are pressurized after receipt at the laboratory if necessary and analyzed using a Gas Chromatography Mass Selective Detector (GC/MSD) in the Selective Ion Monitoring (SIM) mode. The reporting limits for all the compounds are 0.01 parts per billion volume (ppbv).

2. Principle:

Air samples are collected in a summa canister that has been cleaned and under vacuum at 0.05 torr. The air sample is pressurized allowing the contents to flow into the sample concentrator through a mass flow controller and collected on an absorbent tube. The collected compounds are then heated and flushed off the absorbent tube into the GC/MSD for analysis. The confirmation of compound identity with GC/MSD is achieved by retention time and the ratio of selected ions.

3. Safety:

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

3.2 All solvents should be handled with care in a ventilated area.

4. Interferences:

Significant contamination of the analytical equipment can occur whenever samples containing high volatile organic compound concentrations are analyzed. This in turn can result in carryover contamination in subsequent analyses.

Whenever a high concentration (>10 ppbv) sample is encountered, it should be followed by an analysis of blank sample to check for carryover contamination.

5. Apparatus and Equipment:

5.1 Silco steel summa air canisters (Restek # 24142-650).

5.2 Mass flow controller.

5.3 Air concentrator auto sampler (Lotus Consulting).

5.4 Gas chromatograph (Scion 436) equipped with a mass spectrometer (Scion Instruments SQ) or equivalent.

5.5 Analytical column: CP-Select 624 CB 60 m x 0.32 mm 1.8 µm film or equivalent.

5.6 Canister cleaning system (Wasson-ECE TO-Clean) or equivalent.

6. Standards, Reagents and Supplies:

6.1 Calibration air standard purchased from an ISO 17034 accredited vendor containing the following compounds at 100 ppbv:

6.1.1	Bromomethane	CAS Number 74-83-9
6.1.2	cis-1,3-Dichloropropene	CAS Number 10061-01-5
6.1.3	trans-1,3-Dichloropropene	CAS Number 10061-02-6

6.2 Nitrogen gas (Ultra High Purity)

6.3 Helium gas (Ultra High Purity)

All reagents shall meet the minimum requirement for residue and pesticide analysis.

7. Standards Preparation:

Calibration Standards

7.1 Make a 1:100 dilution of the 100 ppbv standard for the calibration standards.

7.2 Use the applicable Scion methods to load varying volumes of the 1.0 ppbv air mixture for the instrument calibration. Suggested Levels are 0.01, 0.05, 0.15, 0.25 and 0.5 ppbv.

8. Sample Preservation and Storage:

All samples shall be stored in the laboratory at ambient temperatures.

9. Test Sample Preparation:

9.1 Sample Preparation:

9.1.1 Total sample volume for all samples using the stated calibration curve will be 1,000 mL.

9.1.2 Sample volumes less than 1,000 mL will be used for high concentration samples or samples with interfering matrices.

10. Instrument Calibration:

10.1 The calibration standard curves consist of five levels. The lowest level must be at or below the corresponding reporting limits.

10.1.1 The current working standard levels are 0.01 ppbv, 0.05 ppbv, 0.15 ppbv, 0.25 ppbv and 0.5 ppbv.

10.2 The calibration curves for the GC/MSD are generally obtained using linear regression. Quadratic fit may be used if the response of certain compounds exhibits quadratic behavior.

10.3 The following amounts of the 1.0 ppbv air mixture will be loaded through the Wasson auto sampler to generate the 5-point calibration curve (all samples are loaded using 1,000 mL which takes 1,200 seconds).

Table 1 – Calibration Levels (Assuming 1,000 mL for All Samples)

Calibration Level	Calibration Amount (ppb)	1.0 ppb Air Mixture Volume (mL)	Sampling Time @ 50mL/min (seconds)
Level 1	0.01	10	12
Level 2	0.05	50	60
Level 3	0.15	150	180
Level 4	0.25	250	300
Level 5	0.50	500	600

11. Instrumental Analysis:

11.1 Injection Scheme:

The GC/MSD may need to be conditioned with a matrix sample or a humidified air blank before running the following sequence:

11.1.1 Set of calibration standards

11.1.2 Air blank

11.1.3 Air spike

11.1.4 Set of up to 12 test samples

11.1.5 Set of calibration standards

11.2 GC/MSD Instrumentation:

11.2.1 Scion Instruments 436 with SQ mass spectrometer and Lotus Consulting air concentrator auto sampler

11.2.2 Column: CP-Select 624 CB 60 m x 032 mm x 1.8 µm film

11.2.3 Injector temperature: 250 °C

11.2.4 Oven temperature:

Table 2 – Oven Temperature Gradient Parameters

Oven Ramp	Program (°C/min)	Temperature (°C)	Hold (min)
Initial	--	-40	7
Ramp 1	20	100	0
Ramp 2	25	250	6

11.2.5 Retention times and ions:

Table 3 – Retention Times and Ions Selected for SIM Acquisition

Compound Name	Retention Time	Selected Ions[1]	Starting Time
Bromomethane	33.9	**94**, 96	3
cis-1,3 Dichloropropene	38.3	**75**, 77, 110	8
trans-1,3 Dichloropropene	38.6	**75**, 77, 110	8

[1] Quantitation ion shown in bold

12. Quality Control:

12.1 Each set of samples shall have a blank and a minimum of one spike sample. Each set contains up to 12 samples.

12.2 The blank shall be free of target compounds above the reporting limit.

12.3 The recoveries of the spike should be within the control limits.

12.4 The retention time shall be within ± 0.1 minute of that of the standard.

12.5 The sample volumes will be reduced if results fall outside the linear range of the standard curve.

12.6 Method Detection Limit:

The method detection limit (MDL) refers to the lowest concentration of analyte that a method can detect reliably. To determine the MDL, 7 replicate air samples at 1.0 ppbv are analyzed. The standard deviation

from the spiked sample recoveries are used to calculate the MDL for each analyte using the follow equation:

$$\mathrm{MDL} = \mathrm{tS}$$

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 replicate used to determine the MDL, t = 3.143.

12.7 Reporting Limit:

The reporting limit (RL) refers to the level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. In general, the RL is chosen in a range 1 – 5 times the MDL. The response reproducibility of each compound is also considered to determine the RL.

MDL data and the RL are tabulated in Appendix I.

12.8 Method Validation Recovery Data and Control Limits:

12.8.1 The method validation consists of 5 sample sets. Each set includes 5 levels (0.01, 0.05, 0.15, 0.25 and 0.50 ppbv).

12.8.2 Upper and lower warning and control limits are set at $\pm$ 2 and $\pm$3 standard deviations of the average % recovery, respectively.

12.8.3 Method validation results and control limits are tabulated in Appendix II.

13. Calculations:

13.1 The quantification is based on the sum of area count of the quantitation ion of the compound analyzed. The calculation is based on external standard (ESTD).

13.2 The correlation coefficient, slope, and intercept of the linear regression line are calculated once the calibration standards are defined. The equation for calculating analytes using a linear calibration is as follows:

$$\mathrm{y} = \mathrm{mx} + \mathrm{b}$$

Where: y = peak response
m = slope
x = concentration of compound
b = intercept

When the unit and the dilution factor are entered correctly in the analysis sequence, the software will then correctly generate the results.

13.3 Results can be manually calculated by a single point standard. The unit is ppbv.

The general equation is as follows:

$$\text{ppbv} = \frac{(\text{sample peak area})\ (\text{standard concentration } ppbv)}{(\text{standard peak area})}$$

13.4 Calculate the pressurization factor (PF) when pressurizing the canister before analysis:

$$\text{PF} = \frac{14.7\ psig + \text{ analysis pressure } psig}{14.7 * [\ 1 - \ (\ \text{receiving vacuum } in.Hg\ /\ 29.9\ in.Hg)\ ]}$$

14. Reporting Procedure:

14.1 Perform quantification with Enhanced Data Analysis software:

Standard Data File

14.1.1 Load a standard data file

14.1.2 Integrate the data file

14.1.3 Edit compounds based on retention time and identity

14.1.4 Review the window range of each compound and adjust it as needed

14.1.5 Reintegrate the data file based on the new method

14.1.6 Update levels

14.1.7 View the calibration curves

14.1.8 Save as a new method

Sample Data File

14.1.9 Load a sample data file

14.1.10 Perform quantification with this new method and new calibration curves

14.1.11 Review each compound and perform integration correction if necessary

14.1.12 Save this reviewed file

14.1.13 Print the reviewed data file

14.2 Acceptance Criteria:

14.2.1 Peak retention time between standards, QC spikes and unknowns shall be within 20 seconds. If there is a known reason for retention time shifting, an explanation memo shall be included.

14.2.2 Peak response shall be within the calibration range.

14.2.3 The R^2 of calibration curve or overlay calibration curves shall be 0.990 or better.

14.2.4 Recoveries of spike QC shall be within the established control range, otherwise a rerun of the entire set shall be performed. If problems remain, an explanation memo shall be included.

14.2.5 The ratio of product ion and precursor ion between standard and unknown shall be consistent and the variation of the ratio between standard and unknown shall be within ± 20%.

14.2.6 Manual single point calculation result is acceptable with explanation if standard and sample areas are within 30% of each other.

14.3 Reporting:

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

14.3.2 Fill out COC, QC sheet, and control chart.

15. Canister Cleaning and Certification

15.1 All canisters must be clean and free of any contamination before sample collection.

15.2 All canisters are leak tested by pressurizing them to 30 psig with zero-air or nitrogen. The pressure should not vary by more than 2 psig over a 24 hour period.

15.3 Canister cleaning:

15.3.1 The canister valve is opened in a fume hood to release the pressurized air in the canister. Place canister in cleaning oven and start the vacuum pump.

15.3.2 The canister is evacuated to 0.05 mTorr for 30 minutes.

15.3.3 The canister is then pressurized with humid air to 30 psig.

15.3.4 Repeat steps 15.3.2 and 15.3.3 two more times for a total of three evacuation/pressurization cycles for each canister.

15.3.5 At the end of the evacuation/pressurization cycles, pressurize the canister to 30 psig with humid zero air.

15.3.6 The canister is now ready for collection of an air sample.

16. References

16.1 Method TO-14A; U.S. EPA Center for Environmental Research Information, Office of Research and Development, U.S. Environmental Protection Agency Cincinnati, OH 45268; January 1999

Appendix I

Method Detection Limit Data and Reporting Limits

Compound	Set 1 (ppbv)	Set 2 (ppbv)	Set 3 (ppbv)	Set 4 (ppbv)	Set 5 (ppbv)	Set 6 (ppbv)	Set 7 (ppbv)	SD	MDL (ppbv)	RL (ppbv)
Bromomethane	0.0485	0.0521	0.0508	0.0513	0.0503	0.0503	0.0469	0.0018	0.00555	0.01
Cis-1,3 Dichloropropene	0.0493	0.0495	0.0502	0.0505	0.0452	0.0453	0.0519	0.0026	0.00815	0.01
Trans-1,3 Dichloropropene	0.0491	0.0493	0.0492	0.0496	0.0456	0.0453	0.0507	0.0021	0.00655	0.01

Definitions
MDL = Method Detection Limit
ppbv = Part per billion volume
RL = Reporting limit
SD = Standard deviation

Appendix II

Method Validation Data and Control Limits

Compound	MV Run	Spike Level 0.01 (ppbv)	0.05 (ppbv)	0.15 (ppbv)	0.25 (ppbv)	0.5 (ppbv)	Control Limits (%)	
Bromomethane	Day 1	88.0	100	96.7	98.4	96.8	Mean:	96.33
	Day 2	95.2	99.6	96.0	90.4	89.6	SD:	6.19
	Day 3	87.9	110	98.7	92.0	94.4	UCL:	114.90
	Day 4	81.2	102	101	95.6	97.4	UWL:	108.71
	Day 5	106	91.6	103	98.4	98.4	LWL:	83.95
							LCL:	77.76
Cis-1,3-Dichloropropene	Day 1	100	95.8	97.3	94.4	96.6	Mean:	99.18
	Day 2	118	101	92.7	101	96.6	SD:	6.20
	Day 3	108	101	96.7	106	98.6	UCL:	117.77
	Day 4	91.3	92.6	92.7	92.8	93.2	UWL:	111.57
	Day 5	98.2	106	103	106	100	LWL:	86.79
							LCL:	80.59
Trans-1,3-Dichloropropene	Day 1	113	98.4	98	95.6	97.6	Mean:	98.32
	Day 2	91.1	101	96	101	96.4	SD:	6.24
	Day 3	96.6	101	95.3	113	98.4	UCL:	117.04
	Day 4	88.5	91	92.7	94.4	93.2	UWL:	110.80
	Day 5	91.9	101	103	108	102	LWL:	85.84
							LCL:	79.60

Definitions
LCL = Lower control limit
LWL = Lower warning limit
MV = Method validation
ppbv = Part per billion volume
% = percent
SD = Standard deviation
UCL = Upper control limit
UWL = Upper warning limit

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Date	What was revised? Why?
5/15/2012	Changed RL to 0.1 ppbv and updated with new MDL and validation results.
11/6/2013	Changed RL to 0.01 ppbv, updated with new MDL and validation results.
3/23/2022	Reformatted the entire document in accordance with web accessibility requirements
	Made editorial revisions throughout the document for improved readability
	Corrected grammatical errors
	Changed instrument to Scion GC/MSD with Lotus Consulting autosampler
	Changed column to CP-Select 624 CB 60 m x 032 mm x 1.8 µm film
	Updated procedures and instrument parameters to reflect use of the Scion GC/MSD
	Added a title to each of the tables in the document
	Added in validation and MDL results for Scion Instrument