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Title: Determination of Acrolein, Iodomethane, Carbon Disulfide, cis-1,3 Dichloropropene, trans-1,3-Dichloropropene, MIBK and Bromomethane 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 lab and analyzed using GC/MSD in the SIM mode. The reporting limits for all the compounds are 1.0 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 compound 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 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 VOC concentrations are analyzed. This in turn can result in carryover contamination in subsequent analyses.
Whenever a high concentration (>25 ppbv of a trace species) sample is encountered, it should be followed by an analysis of humid zero air to check for carry-over 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 (Wasson-ECE)
5.4 Gas chromatograph (Agilent Model 7890) equipped with a mass spectrometer (Agilent model 5975) or equivalent.
5.5 Analytical column: Wasson-ECE proprietary 60m x 0.32mm 1.8µm film.
5.6 Canister cleaning system (Wasson-ECE TO-Clean)
5.7 Tedlar bags (various sizes)

6. Reagents and Supplies: (All reagents shall meet the minimum requirement in residue and pesticide analysis.

6.1 Nitrogen gas UHP
He gas UHP
Medical air
Methylene Chloride

6.2 Standards: An air mixture of the following compounds at 1.0 ppbv and 0.10 ppbv was prepared for calibration.

Acrolein	CAS Number 107-02-8
Iodomethane	CAS Number 74-88-4
Carbon disulfide	CAS Number 75-15-0
Cis-1,3 dichloropropene	CAS Number 10061-01-5
Trans-1,3 dichloropropene	CAS Number 10061-02-6
MIBK	CAS Number 108-10-1
Bromomethane	CAS Number 74-83-9

7. Calibration Standards Preparation:

7.1 Use the Wasson-ECE auto sampler to load varying volumes of the 0.1 ppbv air mixture for the instrument calibration:

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 1000 mL's.

9.1.2 Sample volumes less that 1,000 mL's 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. (The current working standard levels are 1.0 ppbv, 5.0 ppbv, 15.0 ppbv, 25.0 ppbv and 50.0 ppbv.

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

10.3 The following amounts of the 0.1 ppbv air mixture will be loaded through the Wasson auto sampler to generate the 5 point calibration curve.

Calibration amounts assuming 1000 mL's for all samples

Calibration Level	Calibration Amount	0.1 ppb air mixture Volume (mL)	Sampling time@ 30 mL's /min
Level 1	1.0 ppb	10 mL's	20 seconds
Level 2	5.0 ppb	50 mL's	100 seconds
Level 3	15.0 ppb	150 mL's	300 seconds
Level 4	25.0 ppb	250 mL's	500 seconds
Level 5	50.0 ppb	500 mL's	1000 seconds

All samples are loaded using 1000 mL's which takes 2,000 seconds

11 Analysis:

11.1 Injection Scheme

The GC-MS may need to be conditioned with a matrix sample or a humidified air blank before running the following sequence: A set of calibration standards, an air blank, an air spike, a set of up to 12 test samples, then another set of calibration standards.

11.2 GC-MSD Instrumentation:

11.3.1 Agilent GC-MSD model HP7890 with a Wasson-ECE air concentrator auto sampler.
11.3.2 Column: Wasson propriarity 60m x 032mm x 1.8μm film
11.3.3 Temperature program

Injector Temperature: 250 °C
Oven Temperature:

Oven Ramp	Program (°C/min)	Temperature (°C)	Hold (min)
initial		45	4
Ramp 1	15	200	2
Ramp 2	15	250	2

11.3.4 Retention times and ions selected for SIM acquisition:

Compound name	Retention time	Selected ions	Starting time
Bromomethane	4.2	94, 96	3
Acrolein	5.4	55, 56	5
Iodomethane	5.8	142, 127	5
Carbon Disulfide	5.9	76, 78	5
cis-1,3 dichloropropene	10.5	75, 110	10
MIBK	10.6	43, 58	10
trans-1,3 dichloropropene	11.0	75, 110	10

12. Quality Control:

12.1 Each set of samples shall have a humid blank and 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 $\pm$ 20 seconds of that of the standard.

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

12.6 Method Detection Limits (MDL)

The method detection limit 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:

$$MDL = tS$$

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 replicate used to determine the MDL, t=3.143.

12.7 Reporting limit (RL):

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 1.

12.8 Method Validation Recovery Data and Control Limits:

12.8.1 The method validation consisted of five sample sets. Each set included 5 levels (1.0, 5.0, 15.0, 25.0 and 50.0 ppbv)

12.8.2 Upper and Lower warning and control limits are set at ± 2 and ±3 standard deviations of the average % recovery, respectively.

12.8.3 Method validation results and control limits are tabulated in appendix 2.

13. Calculations:

13.1 The quantification is based on the sum of area counts of the product ion and the precursor of the compound analyzed. The calculation is based on external standard (ESTD).

13.2 The correlation coefficient, slope, 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:

$$y = mx + b$$

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

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 (parts per billion volume).

The general equation is as follows:

$$ppbv = \frac{(\text{sample peak area})\ (\text{std. conc. ppbv})}{(\text{std. peak area})}$$

14. Reporting Procedure:

14.1 Perform Quantification with Enhanced Data Analysis software:

14.1.1 Load a standard data file
Integrate the data file
Edit compounds based on retention time and identity
Review the window range of each compound and adjust it as needed.
Reintegrate the data file based on the new method
Update levels
View the calibration curves
Save as a new method

14.1.2 Load a sample data file
Do quantification with this new method with new calibration curves
Review each compound and do integration correction if necessary
Save this reviewed file
Print this 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

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.

14.3.3 Prepare data package. Peer review. Report.

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

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

15.3.2 The canister is evacuated to 0.05mTorr 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 2 more times for a total of three evacuations/pressurizations 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 then analyzed by the GC/MS system. The canister is clean when there are no detected targeted VOC's > 0.5 ppbv.

15.3.7 After the canister passed the analysis return the canister to the cleaning system and evacuate the canister to 0.05 mTorr. Close the valve and remove the canister from the cleaning system.

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

16 References

Method TO-14A
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