California Department of Food and Agriculture
Center for Analytical Chemistry
Environmental Monitoring Section
3292 Meadowview Road
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Title: Determination of MeBr in Air By GC/ECD

1. Scope:

   This method describes the desorption and determination of methyl bromide from SKC Anasorb 747 air sample tubes.

2. Principle:

   Methyl bromide (MeBr) in the air that has been absorbed onto SKC tubes is desorbed with carbon disulfide. Subsequently, MeBr is quantified using a gas chromatograph equipped with a HP-5 megabore column and an electron capture detector (µECD).

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:

   No known matrix interferences cause quantitative problems above the established reporting level.

5. Apparatus and Equipment:

   5.1 Test tubes, 25 mL, with Teflon lined screw cap
   5.2 Brinkmann Bottle Top Dispenser set to dispense 5mL of solvent
   5.3 Assorted pipettes and micro syringes
   5.4 Volumetric flasks
   5.5 Files able to score the sample tubes or a Dremel (an electric rotary flex shaft tool) with ¾" diamond saw
   5.6 Forceps
   5.7 HP 6890 gas chromatograph with ECD.
   5.8 Shaker (Lab-Line Force Orbital Air Shaker or equivalent)

6. Reagents and Supplies

6.1 Sample tube: Anasorb 747 Sorbent Beaded Active Carbon, SKC Cat. No. 226-83
6.2 MeBr, CAS Number 74-83-9
6.3 Carbon disulfide, Sigma-Aldrich, Pesticide Grade or equivalent
6.4 Ice bath

7. Standards Preparation:

7.1 Dilute the 10 mg/mL standard, obtained from the CDFA/CAC Standards Repository, to 1.0 mg/mL, 0.5 mg/mL and 0.1 mg/mL with ethyl acetate to be used for fortification. The working standards shall be prepared to cover the linear range from 0.005 μg/mL to 2.5 μg/mL. The levels prepared were 0.01, 0.025, 0.10, 0.25, 0.50, 1.0, 2.5 μg/mL in CS_2.

7.2 Keep all standards in designated refrigerator for storage.

7.3 The expiration date of each mixed working standard is six months from the preparation date or the same as the stock standards, if sooner.

8. Sample Preservation and Storage:

All samples to be extracted shall be stored in a designated freezer and all sample extracts shall be stored in a designated freezer (0 to -10 ^{o}C).

9. Test Sample Preparation:

9.1 Sample Preparation

9.1.1 Remove samples from freezer to the laboratory bench and allow the samples to warm to near ambient temperature.

9.1.2 Fold a white sheet of 8x11 printer paper into quarters, reopen and place it under the tube to catch any spilled Anasorb.

9.1.3 Score the tube with a file or a Dremel near the empty end of the tube content. Break the tube by holding it with both hands at each side of the cut, having the cut pointing away from you and push the tube by the tips of your thumbs.

9.1.4 Place test tubes containing 5.0 mL of CS_2 in an ice bath.

9.1.5 Use forceps to remove the glass wool plug from the SKC tube and place into a test tube containing the chilled CS_2.

9.1.6 Place the large broken end of the SKC tube in the mouth of the test tube, insert a 9" disposable pipette to push all tube material into the test tube containing 5.0 mL of CS_2 and cap the tube immediately.

9.1.7 Move tubes to a shaker. Allow samples to desorb for 30 minutes while shaking in the shaker.

9.1.8 Pipette the extract in two auto-sampler vials. Cap vials immediately. One vial is for analysis and the other is stored in a designated freezer for possible use later.

9.2 Spike Preparation:

9.2.1 Turn the Airchek Sampler to ON.

9.2.2 Break both ends of a SKC tube with a Dremel.

9.2.3 Place the SKC tube onto the Airchek Sampler with content end first and turn the sampler on.

9.2.4 Use a syringe to spike a known amount of MeBr solution through glass wool onto the Anasorb section.

9.2.5 Pumping for one minute at a flow rate of 100 mL/min.

9.2.6 Follow the steps 9.1.4 through 9.1.8 to extract.

10 Instrument Calibration:

10.1 The calibration standard curve consists of a minimum of three levels. The lowest level must be at or below the corresponding reporting limits.

10.2 The concentrations of the standards used for establishing the calibration curve were 0.01, 0.025, 0.10, 0.25, 0.50, 1.0 and 2.5 μg/mL.

11 Analysis:

11.1 Injection Scheme

Follow the sequence of a set of calibration standards, a matrix blank, solvent blank, a matrix spike, a set test samples, a set of standards, etc.

11.2 Instrumentations and operating conditions:

Agilent 6890 gas chromatograph with dual injectors and dual detectors (μECD)

Column: HP-5 (5% phenyl-methyl polysiloxane) 30m x 0.53 mm x 2.65 μm
Gas Flow: Carrier gas, constant flow (Helium) at 6.8 mL/min
He makeup + carrier flow, 60 mL/min
Temperature: Oven temperature program,
Initial temp.: 45°C for 2 minutes
Rate: 70°C/minute
Final temp.: 230°C for 0.5 minutes
Injector temperature: 220 °C
Detector temperature: 320 °C
Retention time: 1.36 min
Injection Volume: 2.0 μL

12. Quality Control:

12.1 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 SKC tubes samples are spiked with 0.10 μg of MeBr solution. The standard deviation of the findings from the spiked sample are used to calculate the MDL 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.

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

12.2 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. The RL is chosen in a range 1-5 times the MDL, unless otherwise agreed upon by client. The reporting limit for MeBr is 0.1 μg/sample.

12.3 Method Validation:

The method validation consisted of three sample sets. Each set included three levels of fortification (0.1, 1.0 and 10.0 μg/sample) and a method blank.

12.4 Control Chart and Limits:

Control chart was generated using the data from the method validation. The upper and lower warning and control limits are set at ± 2 and 3 standard deviations of the average percentage recovery, respectively, shown in Appendix 2.

12.5 Acceptance Criteria:

12.5.1 Each set of samples will have a matrix blank, solvent blank and a spiked matrix sample.
12.5.2 The retention time should be within ± 2 per cent of that of the standards.
12.5.3 The recoveries of the matrix spikes shall be within the control limits.
12.5.4 The sample shall be diluted if results fall outside of the calibration curve.

13. Calculations:

The quantification is based on an external standard (ESTD) calculation using peak area. The chemstation software used a piecewise curve fit with all levels weighted equally and origin forced.

$$\mu g = \frac{(\text{sample peak area})\ (\text{std. conc. } \mu g/mL)\ (\text{std. vol. injected})\ (\text{sample final vol., (mL)})}{(\text{std. peak area})\ (\text{sample vol. injected})}$$

14. Reporting Procedure:

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

15. Discussion:

DPR substituted SKC Anasorb 747 sampling tubes for the discontinued SKC charcoal tubes which were used before. This method was adopted and validated from OSHA method #PV2040.

It is important that the test tubes which contain carbon disulfide solvent be surrounded with ice when the contents of the SKC tube are transferred. The ice prevents the heat of desorption from vaporizing the methyl bromide out of solution causing it to be lost.

16 References

16.1 United States Department of Labor Occupational Safety & Health Administration, OSHA, *Methyl Bromide* Method # PV2040 (partially validated method).

16.2 Lee, Paul and Lew, Robert; *Determination of Methyl Bromide Desorbed from Charcoal Tubes* 1998, Method # 39.0 Environmental monitoring method, Center for Analytical Chemistry, CDFA.

APPENDIX I

The Method Detection Limit (MDL) data

	MeBr Spiked (μg)	Result (μg)	% Recovery
MDL-spike1	0.1	0.0985	98.5%
MDL-spike2	0.1	0.1041	104%
MDL-spike3	0.1	0.0974	97.4%
MDL-spike4	0.1	0.0949	94.9%
MDL-spike5	0.1	0.0877	87.7%
MDL-spike6	0.1	0.0892	89.2%
MDL-spike7	0.1	0.0903	90.3%
Average		0.09458	
STDEV		0.00590	
MDL=3.143xSTDEV		0.01854	
RL		0.05	

Appendix 2
Method Validation Data for MeBr

Spike Level MeBr Spiked (μg)	**Set1** MeBr Recovery (%)	**Set 2** MeBr Recovery (%)	**Set 3** MeBr Recovery (%)
0.1	96.0	85.4	96.0
1.0	102	115	123
10.0	88.0	97.6	93.2

Average		99.6
Standard Deviation		12.2
Upper warning Limit	2x Stdev	124%
Upper Control Limit	3x Stdev	136%
Lower warning Limit	2x Stdev	75.2%
Lower Control Limit	3x Stdev	62.8%

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