

Appendix M. Chemical Analytical Method  
Methyl bromide – sorbent tubes,  
California Department of Food and Agriculture Laboratory

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### Determination of Methyl Bromide Desorbed from Charcoal Tubes

**Scope:** This method describes the desorption and determination of methyl bromide from charcoal air sample tubes.

**Principle:** Methyl bromide (MeBr) in the air that has been absorbed onto activated charcoal is desorbed from the charcoal with ethyl acetate. Subsequently, MeBr is quantified using a gas chromatograph equipped with a HP-5 megabore column and an electron capture detector (ECD).

#### Reagents, Equipment and Instrument:

##### *Reagents:*

1. Ethyl acetate, Fisher, pesticide grade
2. Methyl bromide, analytical grade
3. Charcoal tubes - SKC #226-38-02 SKC West: phone (714) 992-2780

##### *Equipment:*

1. Test tubes, 25 mL, with Teflon-liner caps
2. Assorted pipettes and micro-syringes
3. Volumetric flasks, 100 mL
4. Small triangular file
5. Thermolyne Vortex Maxi Mixer II
6. Forceps
7. Glass syringe, 5 mL
8. Nylon Acrodisc<sup>®</sup>, 0.2  $\mu$ m, Gelman.
9. Airchek Sampler, Model 224-PCXR7, with a flow about 15 mL/min.
10. ORBO tube cutter, Supelco # 2-0596

##### *Instrument:*

Hewlett Packard 5890 Series II Gas Chromatograph with autosampler and equipped with an (ECD).

**Analysis:***Sample Extraction:*

1. Remove samples from frozen storage. Allow samples to stand at room temperature for 20-30 minutes before starting extraction of methyl bromide.
2. Fold a sheet of white paper into quarters, reopen and place under the test tube to catch spills.
3. Pipette a known volume of ethyl acetate into a labeled test tube. A volume of 10 mL for tube A and 5 mL for tube B is suggested.
4. Remove caps from a charcoal sample tube. Score the tube with a file just above the spring wire and break the glass tube.
5. With a forceps, immediately remove the spring wire only and place it in the test tube containing a known volume of ethyl acetate.
6. Placing the large broken end of the charcoal tube in the mouth of the test tube, insert a Pasteur pipette from the opposite end and push the glass wool and charcoal into the test tube. Immediately cap the test tube.
7. Extract MeBr from charcoal by mixing for 30 seconds using a vortex mixer.
8. Allow the mixture to stand for 3-5 minutes. Filter 1.5 -2 mL of the mixture through a Nylon Acrodisc and collect the extract in an autosampler vial for analysis.
9. If the peak height of the sample is greater than that of the highest standard, dilute the extract and rerun the standards and the diluted extract.

*Preparation of the Blank:*

1. Score a charcoal tube A or B with a file just above the spring wire and break the glass tube.
2. Score the tip of the opposite end of the same tube and break the tube at the end.
3. Follow steps 5-8 under *Sample Extraction*.

*Preparation of the Spike:*

1. Turn the Airchek Sampler to ON for one minute.
2. Break tips of a charcoal tube A with a tube cutter.
3. Place the charcoal end of the tube onto the Airchek Sampler.
4. Place a micro-syringe needle past the spring wire and about 0.5cm below the glass wool. Add 10  $\mu$ L of ethyl acetate containing a known amount of methyl bromide onto the charcoal.
5. For tube B, break the charcoal end with a tube cutter. Score the other end one inch from the tip with a file and break it. Then spike it in a similar manner as for tube A.
6. After running for one minute, score the tube with a file just above the spring wire and break the glass tube.
7. Follow steps 5-9 under *Sample Extraction*.

*Instrument Conditions:*

Hewlett Packard 5890 Series II GC equipped with ECD

Column: HP-5 (5% phenyl-methyl polysiloxane) 30 m x 0.537 mm x 2.65  $\mu$ m

Carrier gas: helium; Flow rate: 7 mL / minute

Injector: 220 °C splitless

Detector: 320 °C

*Instrument Conditions:* continued

Temperature Program: Initial Temp: 45 °C held for 2 minutes  
 Rate: 70 °C / minute  
 Final Temp: 230 °C held for 0.5 minute

Injection volume: 3 µL

Retention time: 1.3 ± 0.1 minute. Retention time may vary depending on GC parameters.

*Alternative Conditions:*

When there is an interfering peak, the following conditions are suggested.

Temperature Program: Initial Temp: 30 °C held for 4 minutes  
 Rate: 50 °C / minute  
 Final Temp. 250 °C held for 0 minute

Retention Time: 1.7 ± 0.1 minute

*Calculations:*

Calculate the amount of MeBr present in a charcoal sample tube as follows:

- without dilution

$$\mu\text{g MeBr} = \frac{(\text{peak ht sample}) (\eta\text{g std injected}) (\text{sample final volume, mL})}{(\text{peak ht standard}) (\mu\text{L injected})}$$

- with dilution

$$\mu\text{g MeBr} = \frac{(\text{peak ht sample}) (\eta\text{g std injected}) (\text{sample final volume, mL})}{(\text{peak ht standard}) (\mu\text{L injected})} \times \text{dilution factor}$$

**Method Performance:***Method Detection Limit:*

Method Detection Limit (MDL) refers to the lowest concentration of analytes that a method can detect reliably in either a sample or blank. To determine the MDL, 7 charcoal tubes were spiked individually with 0.2 µg of MeBr. These spiked samples along with a blank were analyzed using the described method. The standard deviation was computed from the 7 recovered results (µg).

The MDL was calculated using the following equation:

$$\text{MDL} = t_{(n-1, 1-\alpha = 0.99)} S$$

where:  $t_{(n-1, 1-\alpha = 0.99)}$  is the Student 't' value for the 99% confidence level with n - 1 degrees of freedom (for seven replicates, t = 3.143 with 6 degrees of freedom).

n represents the number of replicates.

S denotes the standard deviation obtained from replicate analyses

*Method Detection Limit:* continued

The 7 recovered results, the standard deviations and MDL are:

Sample No.	$\mu\text{g}$ Spiked	$\mu\text{g}$ Recovered
1	0.200	0.205
2	0.200	0.198
3	0.200	0.180
4	0.200	0.192
5	0.200	0.173
6	0.200	0.190
7	0.200	0.184

Standard Deviation = 0.011  $\mu\text{g}$

MDL = 0.035  $\mu\text{g}$ .

*Reporting Limit:*

Reporting Limit (RL) refers to the level above which quantitative results may be obtained. Usually RL is set at one to five times of MDL. In this method the reporting limit is rounded to 0.2  $\mu\text{g}$  per charcoal tube .

*Recovery Data:*

Charcoal tubes were spiked at three different levels of MeBr, 2, 20 and 100  $\mu\text{g}$ . Spiked samples were extracted with ethyl acetate and the 20.0 and 100  $\mu\text{g}$  samples were diluted accordingly.

The amount of MeBr in the extract was subsequently determined. Recoveries of methyl bromide are:

## % Recovery of Spikes

Sample	Spk-2 $\mu\text{g}$	Spk-20 $\mu\text{g}$	Spk-100 $\mu\text{g}$
1	75.2	78.7	80.1
2	68.7	66.0	76.6
3	78.7	78.6	75.4
4	77.2	77.8	77.7
5	71.1	77.1	76.1

**Discussion:**

High humidity may affect trapping efficiency. When the amount of water in the air is so large that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Experiments using toluene indicate that high humidity severely decreases the breakthrough volume<sup>(2)</sup>.

Check each bottle of ethyl acetate on the GC for any interfering peaks before using for extracting samples. Any bottle of ethyl acetate found to contain interfering peaks is unsuitable for use in this work.

Methyl bromide is highly volatile. Consequently on extraction of MeBr, test tubes must be tightly capped. **Do Not Use Caps Without A Teflon Liner.**

**Discussion:** continued

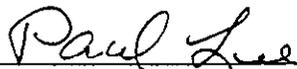
Each analytical run contained standards ranging from approximately 0.04 to 2 µg/mL (eg. 0.04, 0.08, 0.16, 0.32, 0.64 and 1.2 µg/mL). This range of 5-6 standards was run after every ten samples. When considering a longer pump running time (60 minutes), the results of six spikes (5 µg methyl bromide) gave an average recovery of  $76.3 \pm 3.4\%$ , quite comparable with the above results (September 25, 1998).

**References:**

1. *NIOSH Manual of Analytical Methods, Second Edition Method S372*. Available from Superintendent of Documents, US. Government Printing Office, Washington, DC, 20402.
2. Fredrickson, Scott A., *Determination of EDB on Charcoal Tubes*, 1979, Worker and Safety Methods, California Department of Food and Agriculture, Chemistry Laboratory Services, 3292 Meadowview Road, Sacramento, California 95832.
3. Malone, B., *Analysis of Grains for Multiple Residues of Organic Fumigants*. AOAC, 52, p. 800, 1969.
4. Clower, M., *Modification of the AOAC Method for Fumigants in Wheat*, FDA Laboratory Information Bulletin #2169, August, 1978.
5. Fredrickson, Scott A., private communication, CDFA Work Health and Safety, California Department of Food and Agriculture, Chemistry Laboratory Services, 3292 Meadowview Road, Sacramento, California 95832

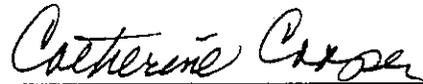
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