California Department of Food and Agriculture
Center for Analytical Chemistry
Environmental Analysis Section
3292 Meadowview Road
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Title: Determination of Iodomethane Desorbed from Charcoal Tubes

1. **Scope**:

This section method (SM) provides stepwise procedure for the desorption and determination of Iodomethane in charcoal air sample tubes. It is followed by all authorized EA personnel.

2. **Principle**:

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

3. **Safety**:

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

4. **Interferences**:

There were no matrix interferences that caused quantitative problems during method development and validation. Each lot of ethyl acetate was check for interfering peaks before using to extract samples.

5. **Apparatus and Equipment**:

5.1 Airchek Sampler, Model 224-PCXR7, with a flow of 1L/min
5.2 Dremel, Multipro Model # 395 Type 5
5.4 Vortex-vibrating mixer
5.5 Gas Chromatograph equipped with an electron capture detector (ECD)
5.6 Forceps

6. **Reagents and Supplies**:

6.1 Iodomethane : CAS# 74-88-4
6.2 Ethyl acetate, nanograde or equivalent pesticide grade
6.3 Test tubes, 25 mL, with Teflon-liner caps
6.4 Volumetric Pipette, 10 mL

6.5 Charcoal tubes – SKC #226-16-02
6.6 Recommended analytical column:
(5% Phenyl-methylpolysiloxan) (HP-5 or equivalent) fused silica column, 30m x 530 µm x 2.65-µm film thickness.
6.7 Nylon Acrodics®0.2 µm , Gelman

7. Standards Preparation:

7.1 The Iodomethane stock standard of 30 mg/mL was obtained from the CDFA/CAC Standards Repository. The standard was diluted to 10 mg/mL, 5 mg/mL and 0.5 mg/mL with ethyl acetate for spiking validation purposes.

The working standards were prepared at the following concentrations: 5, 2.5, 1.0, 0.5, 0.25, 0.1, 0.025, and 0.01 µg/mL in ethyl acetate for use in GC instrument calibration.

7.2 Keep all standards in the designated refrigerator for storage.

7.3 The expiration date of each standard is six months from the preparation date.

8. **Sample Preservation and Storage**:

Store all samples waiting for extraction in a separate refrigerator (0 - 5 °C).

9. **Test Sample Preparation**:

9.1 Background Preparation

The Department of Pesticide Regulation (DPR) provided the Charcoal tubes(SKC # 226-16-02) to be used in method validation and QC.

9.2 Preparation blank and spike

Matrix blank: Cut end of charcoal tube just above wire spring and tip of opposite end off. Follow steps 9.3.5 -9.3.8 after adding 10 mL ethyl acetate to test tube.

Matrix spike: Turn the Airchek sampler to on. Cut tips of charcoal tube with a dremel. Place the charcoal end of the tube onto the Airchek Sampler. Use a

syringe to spike a known amount of Iodomethane about 0.5cm below the glass wool and pump for 1 minute. Follow steps 9.3.2- 9.3.8

9.3 Test Sample Extraction

9.3.1 Remove samples from frozen storage. Allow samples to stand at room temperature for 20-30 minutes before starting extraction of Iodomethane.

9.3.2 Fold a white sheet of 8 X 11 printer paper into quarters, reopen and place it under the tube to catch any spilled charcoal.

9.3.3 Pipette 10 mL of ethyl acetate into a labeled test tube.

9.3.4 Remove caps from a charcoal sample tube. Use a Dremel to cut just above the wire spring.

9.3.5 Remove the wire spring and glass wool with forceps and place in the test tube.

9.3.6 Placing the large broken end of the charcoal tube in the mouth of the test tube containing the ethyl acetate, insert a Pasteur pipette from the opposite end and push the glass wool and charcoal into the test tube. Immediately cap the test tube.

9.3.7 Extract the Iodomethane from the charcoal by mixing for 30 seconds using a vortex mixer.

9.3.8 Allow the mixture to stand for 3-5 minutes. Fliter 1.5- 2 mL of the mixture through a 0.2 -µm nylon Acrodisc and collect the solution in two auto sampler vials. Cap them immediately. Store one vial in a designated freezer for possible later analysis.

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 limit.

10.2 The calibration curve for the ECD was obtained using linear regression.

11. **Analysis:**

11.1 Injection Scheme

Follow the sequence of standard curve, ethyl acetate, matrix blank, matrix spike, test samples (maximum of 10-12) and standard curve.

11.2 GC-ECD instrumentation:

11.2.1 Analyze the Iodomethane extracts by a gas chromatography equipped with electron capture detector (ECD).

11.2.2 Recommended temperature program: initial column temperature 45 °C, hold 2 min., ramp at 60 °C/min. to temperature of 250 °C and hold for 4.5 min.

Injector Temperature: 220 °C
Injection volume: 2 uL.

12. **Quality Control**:

12.1 Method Detection Limits (MDL)

Method Detection Limit (MDL) refers to the lowest concentration of the analyte that a method can detect reliably. To determine the MDL, 7 charcoal samples are spiked at 0.1ug and processed through the entire method along with a blank. The standard deviation derived from the spiked sample recoveries was used to calculate the MDL for each analyte using the following 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 replicates 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)

Reporting limit (RL) refers to a 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, as per client agreement. The reporting limit for Iodomethane is 0.05 ug/sample.

12.3 Method Validation

The method validation consisted of three sample sets. Each set included four levels of fortification and a method blank. All spikes and method blanks were processed through the entire analytical method. Spike levels and recoveries for Iodomethane are shown in Appendix 2.

12.4 Control Charts and Limits

Control charts were generated using the data from the method validation for each analyte. The upper and lower warning and control limits are set at ± 2 and 3 standard deviations of the average percent recovery, respectively, shown in Appendix 2.

12.5 Acceptance Criteria

12.5.1 Each set of samples will have a matrix 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:**

Quantitation is based on an external standard (ESTD) calculation using either the peak area or height. The ECD software used a linear curve fit, with all levels weighted equally. Alternatively, at the chemist's discretion, sample results may be calculated using the response factor for the standard.

$$\mu g = \frac{(\text{sample peak area or ht}) \times (\text{std conc.}) \times (\text{std vol. Injected}) \ (\text{sample final vol.(mL)})(1000\ \mu L/mL)}{(\text{std. peak area})(\text{sample vol. injected})(1000 \eta g/\mu g)}$$

14. Reporting Procedure:

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

15. Discussion:

15.1 Three different SKC charcoal tubes (SKC-226-09, 226-16, 226-16-02) were provided by DPR at the start of the project for a preliminary trapping efficiency study. It was done at a rate of 1L/min. for ten hours. SKC -226-16-02 had acceptable recoveries.

15.2 Upon transferring the charcoal to the ethyl acetate it was noticed that the desorption process produced heat. The question was raised whether the release of heat could reduce the recovery. The extraction procedure was repeated again, this time placing the tubes containing the ethyl acetate on ice. The recovery didn't improve. Then Iodomethane spiked samples were also processed using the OSHA method PV2040, where the charcoal is extracted on ice using carbon disulfide and allowed to desorb by shaking for 30 minutes. Recovery still didn't improve.

16. References:

16.1 Lee, Paul *Determination of Methyl Bromide Desorbed from Charcoal Tubes* Method #39.0,revised 1998, California Department of Food and Agriculture, Center for Analytical Chemistry, Environmental Monitoring Laboratory, 3292 Meadowview Road, Sacramento, California 95832

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

Appendix 1

The Determination of Method Detection Limit (MDL) and Reporting Limit (RL)

Spike	Spike Amount	µg Iodomethane
MDL spk 1	0.1 µg	0.085
MDL spk 2	0.1 µg	0.073
MDL spk 3	0.1 µg	0.084
MDL spk 4	0.1 µg	0.079
MDL spk 5	0.1 µg	0.092
MDL spk 6	0.1 µg	0.087
MDL spk7	0.1 µg	0.079
	SD	0.00577
	MDL	0.0181
	RL	0.05

Appendix 2

Method Validation Data and Control Limits

	Spike level ug/sample	Recovery (%)
Set 1	0.5	65.4
	2.0	76.6
	20	67.4
	100	69.6
Set 2	0.5	65.0
	2.0	62.5
	20	61.0
	100	63.2
Set 3	0.5	79.6
	2.0	71.0
	20	66.5
	100	67.9
Average	X	67.98
Standard Deviation	SD	5.55
UCL	X + 3*SD	84.62
UWL	X + 2*SD	79.07
LWL	X - 2*SD	56.87
LCL	X - 3*SD	51.32

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