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Method of Test for Pesticide Residues in Foods – Test of Methyl Bromide, a Fumigant (2)

1. Scope

This method is applicable for the determination of methyl bromide in fruits, vegetables and crops.

2. Method

After pretreatment, methyl bromide is determined by gas chromatography/mass spectrometry (GC/MS) with headspace injection (HS).

2.1. Equipment

2.1.1. Gas chromatograph/mass spectrometer.

2.1.1.1. Ion source: electron ionization, EI.

2.1.1.2. Column: DB-624 UI capillary column, 1.4 μm, 0.25 mm × 60 m, or an equivalent product.

2.1.1.3. Liner: Agilent P/N 5190-4047, ultra inert, straight, 1 mm, or an equivalent product.

2.1.2. Headspace sampler: XYZ robotic autosampler, shaking speed ≥ 250 rpm, temperature control ≥ 70℃.

2.1.3. Grinder.

2.2. Chemicals

Methanol, HPLC grade;

Deionized water, resistivity ≥ 18 MΩ·cm (at 25℃);

Methyl bromide, 100 μL/mL in methanol, reference standard.

2.3. Apparatus

2.3.1. Headspace vial: 20 mL, glass, with a pre-assembled magnetic steel screw cap and a PTFE/silicone septum.

2.4. Standard solution preparation

Take appropriate amount of methyl bromide reference standard, and dilute with methanol to 10 μg/mL as the standard solution.

2.5. Sample solution preparation

Homogenize the sample using dry ice. After the dry ice is completely sublimated, transfer about 1 g of the sample accurately weighed into a headspace vial, add 15 mL of deionized water, and immediately close the cap as the sample solution.

2.6. Standard curve preparation

Transfer 5-50 μL of the standard solution to each headspace vial, add appropriate amount of deionized water respectively to achieve a final volume of 15 mL, and close the caps immediately as the standard solutions. Operate HS-GC/MS according to the following conditions. Establish the standard curve of methyl bromide by the peak areas of methyl bromide vs. the added concentrations (0.05-0.5 μg).

Headspace sampler operating conditions(note 1):

Incubation temperature: 70℃.

Incubation time: 10 min.

Shaking speed: 250 rpm.

Shaking interval: 60 sec followed by a 30 sec rest.

Syringe temperature: 75℃.

Injection volume: 0.5 mL.

GC/MS operating conditions(note 1):

Column: DB-624 UI capillary column, 1.4 μm, 0.25 mm × 60 m.

Column temperature:

Initial temperature: 35℃, 3 min;

Temperature rising rate: 20℃/min;

Middle temperature: 90℃, 2 min ;

Temperature rising rate: 100℃/min;

Final temperature: 200℃, 2 min.

Carrier gas and flow rate: helium, 1 mL/min.

Injector temperature: 110℃.

Injection mode: split, 40:1.

Interface temperature: 235℃.

Ion source: EI, 70 eV.

Ion source temperature: 230℃.

Detection mode: selected ion monitoring (SIM). Detection ions are shown as follows:

Analyte	Detection ion (*m/z*)
Methyl bromide	94*
	96
	79

*The quantitative ion.

Note 1: All the parameters can be adjusted depending on the instruments used if the above conditions are not applicable.

2.7. Identification

Place the headspace vials with the sample solution and the standard solutions on the headspace sampler, and operate according to the conditions described in section 2.6. Identify methyl bromide based on the retention time and the relative ion intensities(note 2).

Note 2: Relative ion intensities are calculated by peak areas of qualitative ions divided by peak areas of quantitative ions (≤ 100%). Maximum permitted tolerances of relative ion intensities are as follows:

Relative ion intensity (%)	Tolerance (%)
> 50	± 10
> 20～50	± 15
> 10～20	± 20
≤ 10	± 50

2.8. Quantification

The standard addition method is used to quantify the amount of methyl bromide in the sample which is estimated by the standard curve. The sample which was found to contain methyl bromide was prepared as the sample solution described in section 2.6, add the standard solutions which are equivalent to 0-3 times of the estimated concentration of methyl bromide in the sample, and deionized water to achieve a final volume of 15 mL, close the caps immediately, and operate according to the conditions described in section 2.6. Establish a linear regression curve ($y = mx + n$) as Figure 1 based on the peak areas of methyl bromide vs. the added concentrations. Calculate the amount of methyl bromide in the sample by the following formula:

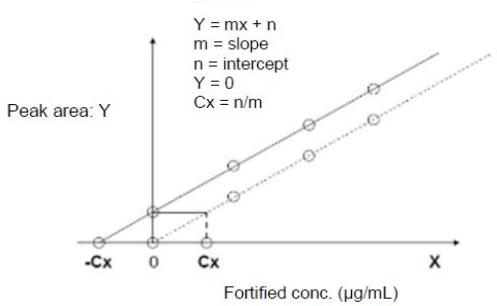

Figure 1. Linear regression curve of the standard addition method

The amount of methyl bromide in the sample (ppm) = $\frac{C}{M}$

Where,

C: the concentration of methyl bromide in the sample solution calculated from n/m (µg)

M: the weight of the sample (g)

Remark

1. Limit of quantification (LOQ) for methyl bromide is 0.05 ppm.
2. Further validation should be performed when interfering compounds are found in the samples.

Reference

1. Du, X., Zhang, W., Liu, B., Liu, T., Xiao, Y., Taniguchi, M. and Ren, Y. L. 2019. Optimization and validation of HS-SPME-GCMS method for determination of multifumigant residues in grain, oilseeds, nuts, and dry fruit. J. AOAC Int. 102: 1877-1883.
2. Zhang, D., Zhu, Q., Li, Z., Chai, Y. and Chen, H. 2023. Determination of methyl bromide residues in tea by headspace solid-phase microextraction coupled with gas chromatography-mass spectrometry. Beverage Plant Res. 3(1): 2.

Reference chromatogram

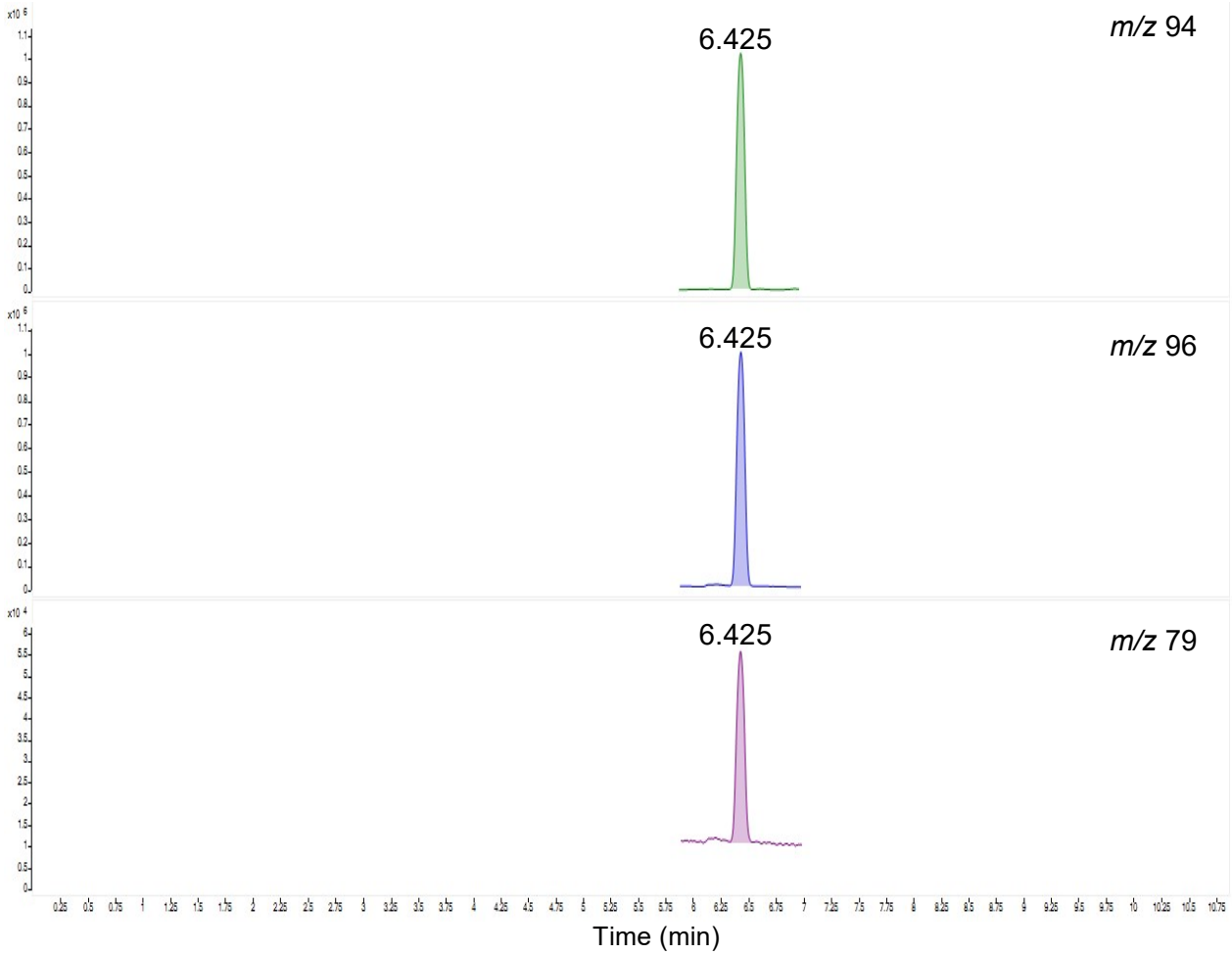

Figure. SIM chromatograms of methyl bromide standard analyzed by GC/MS.