Application Note

Food

Estimation of Methyl Bromide Residues in Food

Using the Agilent 8890 GC and Agilent 7010 triple quadrupole GC/MS system with Agilent 8697 headspace sampler

Authors

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Abstract

This application note demonstrates the use of an Agilent 8890 GC system coupled with an Agilent 8697 headspace sampler and Agilent 7010 triple quadrupole GC/MS system to detect and quantify methyl bromide residues in rice, cumin powder, and red chili powder. The sample was placed into a headspace vial. Milli-Q water was added, the vial was crimped and put into an Agilent headspace sampler, and GC/MS/MS analysis was performed. A limit of quantification (LOQ) of 5 ng/g was achieved in rice, cumin powder, and red chili powder matrices. Average recoveries ranged from 85 to 116%.

Introduction

Bromomethane (methyl bromide) is a halogenated hydrocarbon with a boiling point of 3.6 °C. It is widely used as a fumigant due to its strong fumigation and penetration effects, effectively controlling pests.[1] However, methyl bromide is harmful to the ozone layer, causes environmental pollution, and is harmful to humans.[2] By 2015, most countries phased out its production and application, except for essential uses such as port quarantine. China stopped agricultural use of methyl bromide by the end of 2018.[2] Despite its high volatility, residues of methyl bromide can persist in foods such as nuts and seeds. Therefore, quantitative methods for determining these residues are important. Gas chromatography (GC) is commonly used for analysis, either directly with headspace sampling, or with sample pretreatment methods including solvent extraction and solid phase microextraction. Various detectors are used with GC, such as the flame ionization detector, electron capture detector, and electron ionization. Detection can also be performed by mass spectrometer, using an electron ionization (EI) source. The maximum residue limit for methyl bromide in the EU is 10 ng/g, according to EU Regulation number 396/2005.

In this application note, an Agilent 8697 headspace sampler was used for sample introduction to an Agilent 8890 GC system coupled with an Agilent 7010 triple quadrupole GC/MS for quantification of methyl bromide residues.

Instrument parameters

Table 1. HS-GC/TQ parameters.

Parameters	Values
Headspace Method Parameters	
Incubation Temperature	50 °C
Incubation Time	15 min
Loop Temperature	60 °C
Transfer Line Temperature	70 °C
Loop Size	1 mL
Pressurization Gas	Nitrogen
GC Cycle Time	21 min
GC/MS/MS Method Parameters	
Inlet Temperature	100°C
Analytical Column	Agilent J&W DB-VRX (60 m × 250 µm, 1.4 µm) (p/n 122-1564)
Post-Column	Deactivated Fused Silica Capillary (1 m × 0.15 mm)
PSD 1 Pressure	1 psi
Column Flow	Hydrogen; 1.2 mL/min, constant flow
Injection Mode	Split (10:1)
Oven Program	45 °C (hold 2.0 min), 4 °C/min to 65 °C, 40 °C/min to 245 °C, Hold 4 min
MS Parameters	
Ionization Mode	EI
Ion Source Temperature	230 °C
Quadrupole Temperature (Q1 and Q2)	150 °C
SIM Mode Ions	
Quantifier Ion	96
Qualifier Ions	95, 94, 93

Experimental

Standard preparation

A reference stock solution of methyl bromide (1,000 µg/mL) obtained from Sigma-Aldrich was used to prepare an intermediate stock solution of 1 µg/mL in methanol.

Five prespiked matrix calibration levels were prepared in 20 mL headspace vials by adding the methyl bromide stock solution to 0.5 gram blank matrix of rice, cumin powder, and red chili powder, respectively. 5 mL of Milli-Q water was added to each calibration level, and the vial was immediately crimped, followed by a run on the headspace sampler. The final concentrations are listed in Table 2.

Table 2. Preparation of prespiked matrix calibration.

Calibration Level	Stock Solution Volume (µL)	Blank Matrix (g)	Milli-Q Water Volume (mL)	Prespiked Concentration (ng/g)
L1	2.5	0.5	5	5
L2	5	0.5	5	10
L3	10	0.5	5	20
L4	25	0.5	5	50
L5	50	0.5	5	100

Sample preparation

Approximately 0.50 (± 0.01) g of each sample was weighed into 20 mL headspace vials. 5.0 mL of Milli-Q water was added, and the vial was crimped, immediately followed by a run on the headspace sampler.

Results and discussion

Calibration

Figures 1 through 3 show the linearity of the methyl bromide calibration curve in rice, cumin powder, and red chili powder, respectively. The R^2 obtained was above 0.998.

Repeatability

The repeatability of this method was demonstrated by injecting six replicates of rice, cumin, and red chili powder spiked with 10 ng/g of methyl bromide. The area %RSD and retention time %RSD results are shown in Table 3.

Recovery

Methyl bromide was spiked in samples of rice, cumin, and red chili powder at concentration levels of 10 ng/g. Acceptable recoveries were obtained by quantification through prespike matrix-based calibration. Results are highlighted in Table 4.

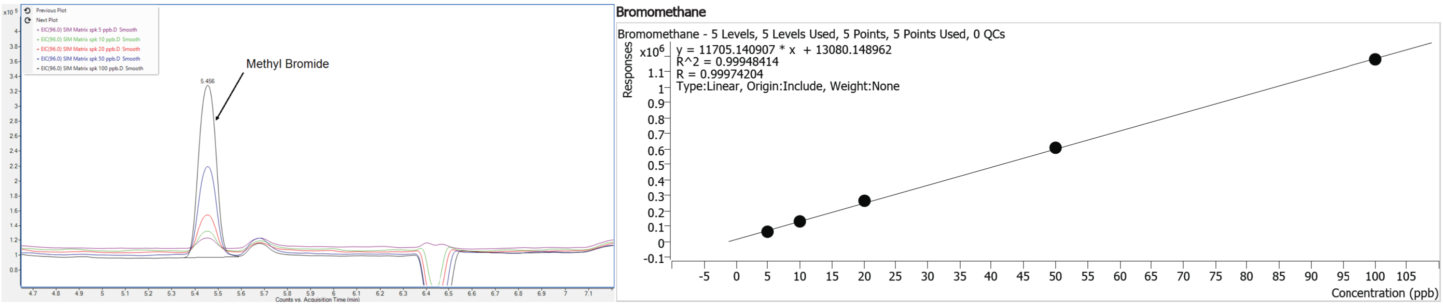

Figure 1. Overlaid chromatograms and calibration curve for prespike matrix standards from 5 to 100 ng/g in rice.

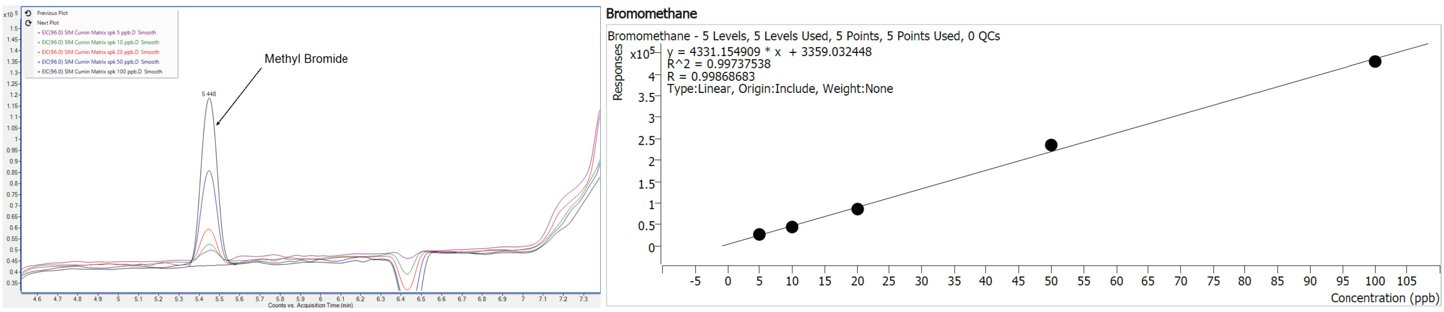

Figure 2. Overlaid chromatograms and calibration curve for prespike matrix standards from 5 to 100 ng/g in cumin powder.

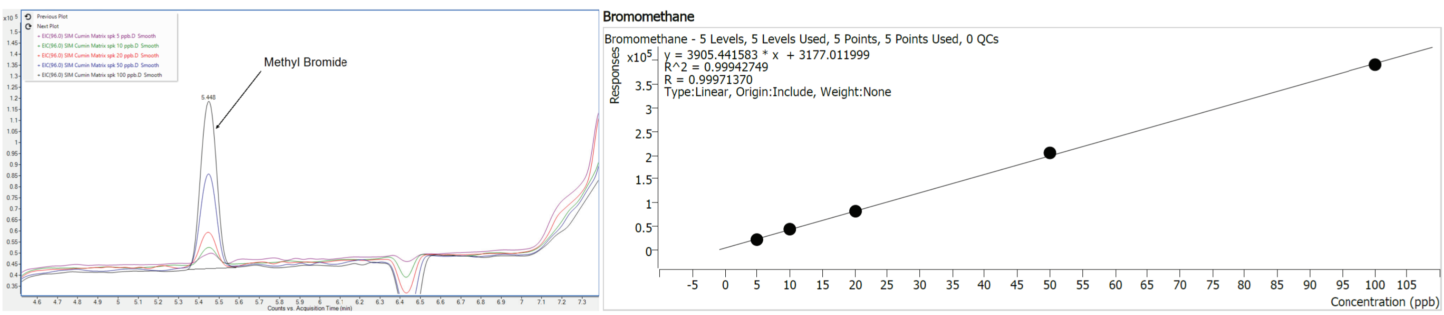

Figure 3. Overlaid chromatograms and calibration curve for prespike matrix standards from 5 to 100 ng/g in red chili powder.

Quantifier and qualifier peaks in matrix standards

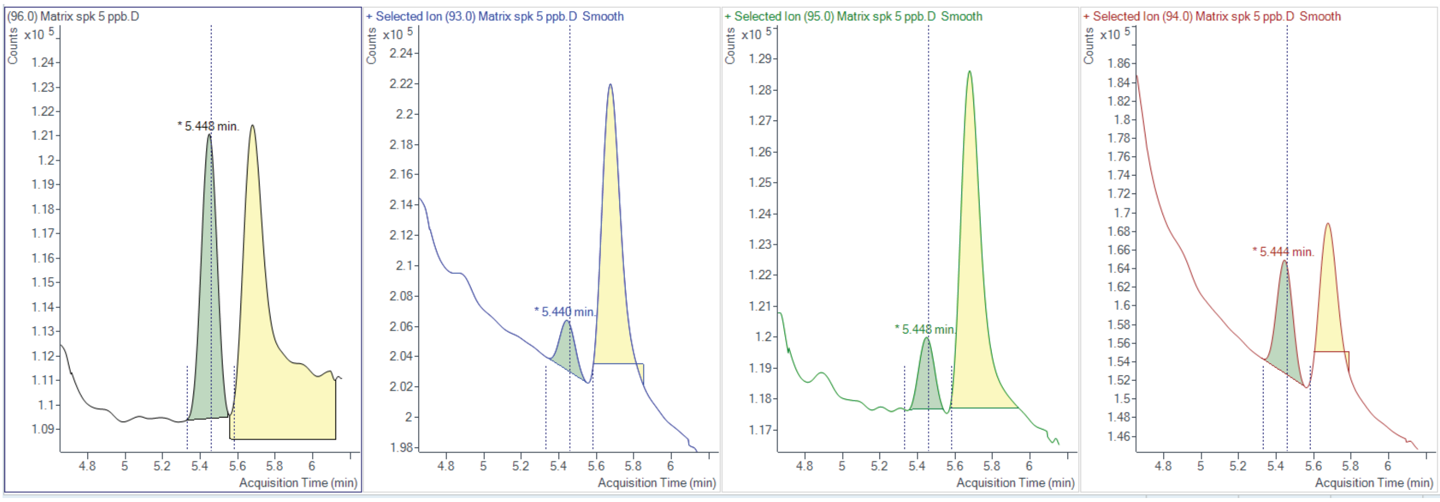

Figure 4. Quantifier and qualifier peaks in 5 ng/g prespike matrix standard in rice.

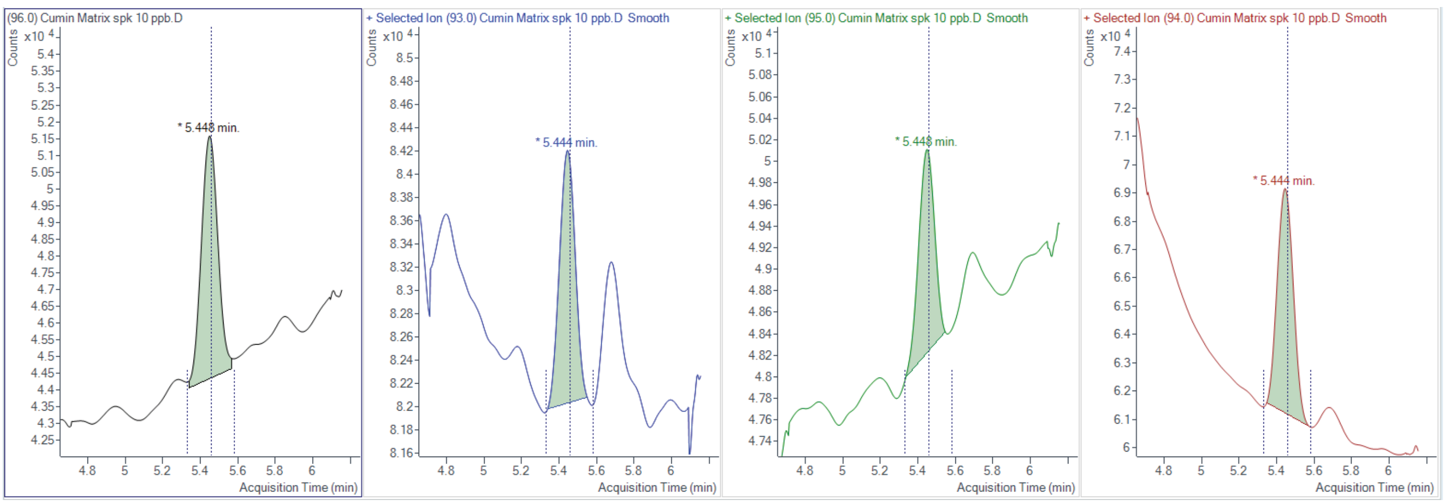

Figure 5. Quantifier and qualifier peaks in 10 ng/g prespike matrix standard in cumin powder.

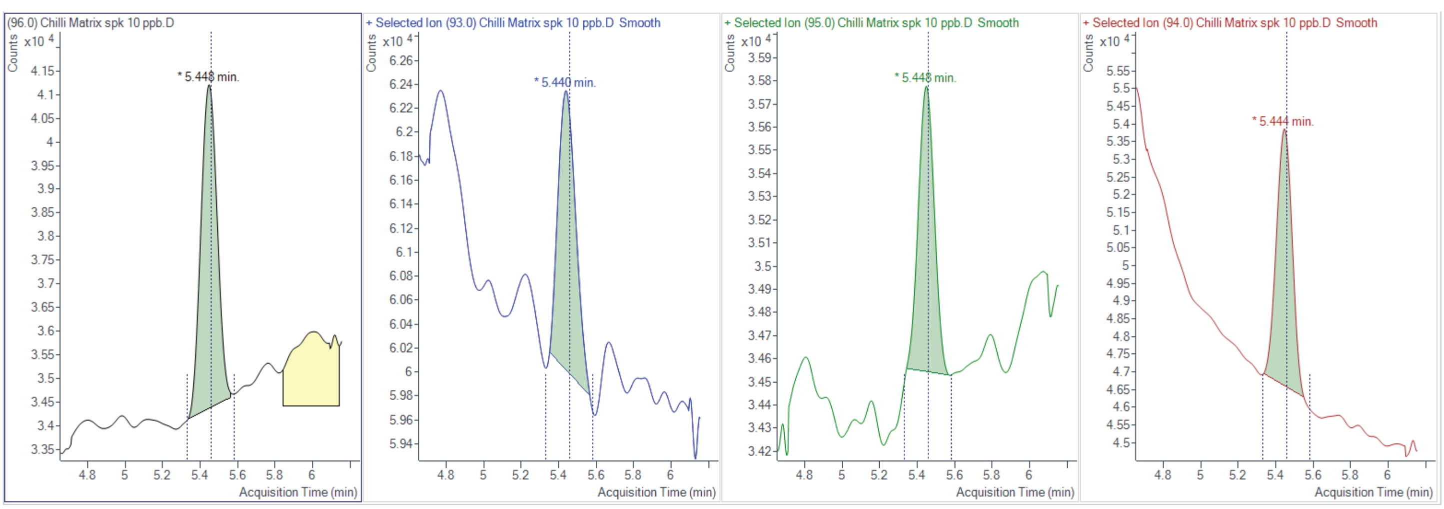

Figure 6. Quantifier and qualifier peaks in 10 ng/g prespike matrix standard in red chili powder.

Table 3. %RSD for six replicates of 10 ng/g prespike matrix standard in rice, cumin powder, and red chili powder.

Number of Replicates	Rice		Cumin Powder		Red Chili Powder	
	RT (min)	Area Counts	RT (min)	Area Counts	RT (min)	Area Counts
10 ng/g Matrix Standard Replicate - 1	5.452	151383	5.448	42440	5.448	41588
10 ng/g Matrix Standard Replicate - 2	5.451	155188	5.448	41917	5.448	38957
10 ng/g Matrix Standard Replicate - 3	5.452	148147	5.456	38916	5.448	42988
10 ng/g Matrix Standard Replicate - 4	5.452	150417	5.452	39040	5.448	40472
10 ng/g Matrix Standard Replicate - 5	5.452	140557	5.448	40337	5.448	40746
10 ng/g Matrix Standard Replicate - 6	5.452	143079	5.448	38670	5.448	41553
Mean	5.452	148128.500	5.283	40220.000	5.448	41050.667
SD	0.000	5449.605	0.407	1632.006	0.000	1349.477
%RSD	**0.007**	**3.679**	**0.061**	**4.058**	**0.000**	**3.287**

Table 4. Percent recovery of methyl bromide in rice, cumin powder, and red chili powder spiked at the 10 ng/g level.

Food Matrix	Methyl Bromide		
	Spiked Concentration (ng/g)	Average Obtained Concentration (ng/g)	Recovery (%)
Rice	10	11.625	116.25
Cumin Powder	10	8.511	85.11
Red Chili Powder	10	10.044	100.44

Conclusion

An accurate and rugged method was developed which meets the requirements of the EURL for the maximum residue limit of methyl bromide in foodstuffs. This ranges from 10 to 100 ng/g, depending on the commodity (Reg. (EC) number 396/2005) for the analysis of pesticides in rice, cumin powder, and red chili powder. The LOQ of the method was demonstrated at 5 ng/g for all tested matrices. Repeatable results were found for six successive replicates of matrix-based standards at 10 ng/g concentration levels. Sufficient recoveries were obtained in all tested matrices at 10 ng/g spiked concentration levels. Thus, this study demonstrates the applicability of this method for routine analysis of food samples for methyl bromide at trace levels.

References

1. Zhang, D.; Zhu, Q.; Li, Z.; Chai, Y.; Chen, H. Determination of Methyl Bromide Residues in Tea by Headspace Solid-Phase Microextraction Coupled with Gas Chromatography-Mass Spectrometry. *Beverage Plant Res.* **2023**, *3*. https://doi.org/10.48130/BPR-2023-0002
2. Yates, S. R.; Gan, J.; Papiernik, S. K. Environmental Fate of Methyl Bromide as a Soil Fumigant. *Reviews of Environmental Contamination and Toxicology*; Ware, G. W., Ed.; Springer: New York, 2003, Vol. 177; pp 45–122. https://doi.org/10.1007/0-387-21725-8_2

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