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Application News

GC-MS AOC-6000 Plus / GCMS-TQ™8040 NX

Simultaneous Analysis of Methoxypyrazines in Processed Tomato Products by GC–MS/MS with SPME Arrow

Yusuke Takemori[1], Toshinari Ishii[1], Yuto Nakasuji[1], Kaho Kato[2], Nahoko Shinohara[2], Yasuko Omori[2], Takayo Terada[2], Kiyoshi Tanaka[2]

1 Shimadzu Corporation, 2 KAGOME CO.,LTD.

User Benefits

- SPME Arrow enables high-sensitivity determination of methoxypyrazines in processed tomato products by efficiently preconcentrating volatile compounds.
- GC–MS/MS in MRM mode provides isomer selectivity and reliable quantitation of methoxypyrazines, even in complex sample matrices.
- The AOC-6000 Plus multifunctional autosampler automates SPME Arrow injection to increase throughput and improve repeatability.

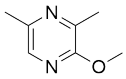
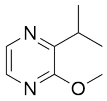
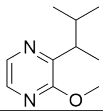
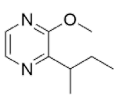
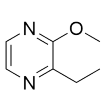
■ Introduction

In processed vegetable foods and beverages, small changes in aroma and flavor can strongly affect perceived quality. For processed tomato products in particular, a vegetative (green) or hay-like off-flavor is often a key concern. This off-flavor has been linked to methoxypyrazines present at very low levels (ppt levels around 10 ng/L).

Methoxypyrazines include many closely related analogs. Therefore, a robust quantitative method must deliver both high sensitivity and sufficient selectivity (and/or separation) to handle real matrices.

In this article, five methoxypyrazines previously detected in vegetables (Table 1) were analyzed using a GC-MS/MS system with the SPME Arrow injection method. The method provides stable quantitation at ng/L (ppt) levels, even in complex, interference-rich samples.

Table 1 Five Target Methoxypyrazines

Target Compounds	Structures
2-methoxy-3,5-dimethylpyrazine (MDMP)	
2-isopropyl-3-methoxypyrazine (IPMP)	
2-isobutyl-3-Methoxypyrazine (IBMP)	
2-sec-butyl-3-methoxypyrazine (SBMP)	
2-ethyl-3-methoxypyrazine (EMP)	

■ System Configuration

All measurements were performed with a GCMS-TQ8040 NX triple quadrupole GC–MS/MS system equipped with an AOC-6000 Plus multifunctional autosampler (Fig. 1).

The AOC-6000 Plus supports multiple sample introduction techniques—including liquid injection, headspace, and SPME—and can switch between them automatically based on the method. This flexibility makes it well suited for laboratories that handle many sample types and applications.

Fig. 1 AOC-6000 Plus + GCMS-TQ™ 8040 NX

■ Optimizing Sample Introduction for Maximum Sensitivity

To detect ppt-level (ng/L) of methoxypyrazines, sensitivity was enhanced using the following strategies:

- Use an SPME Arrow to preconcentrate volatile compounds.
- Select an SPME phase appropriate for methoxypyrazines (nitrogen-containing analytes).
- Optimize the GC inlet split ratio.
- Add NaCl (1 g/mL) to promote salting-out.

With an SPME Arrow (DVB/PDMS), methoxypyrazines at 10 ng/L were detectable. Fig. 2 compares IBMP responses obtained under different split ratios and with/without salting-out. Combining salting-out with split optimization further increased sensitivity.

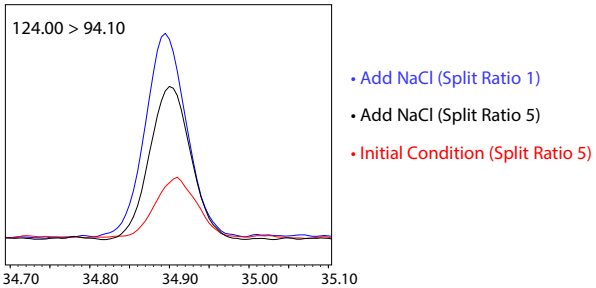


Fig. 2 Comparison of MRM Chromatograms for a 10 ng/L IBMP Standard

■ Isomer Selectivity Using MRM

Methoxypyrazines include many structural analogs. MDMP and EMP are isomers with the same molecular weight and similar mass spectra (Fig. 3). They are also difficult to separate by GC alone, which has made simultaneous analysis challenging with conventional approaches.

To differentiate these isomers by mass spectrometry, compound-specific MRM transitions were evaluated. Fig. 4 shows MRM chromatograms for 10 ng/L MDMP and EMP-spiked ultrapure water. The selected quantifier transitions provided analyte-specific detection for each compound.

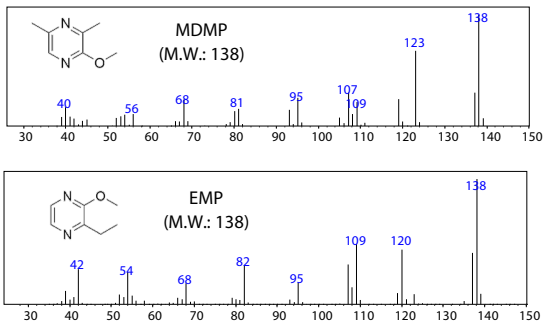


Fig. 3 EI Mass Spectra of MDMP and EMP

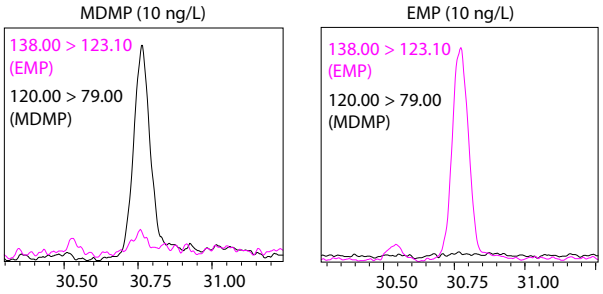


Fig. 4 MRM Chromatograms of MDMP and EMP (10 ng/L)

■ Analysis Conditions

Tables 2 and 3 summarize the method parameters.

Table 2 System Configurations and Analysis Conditions

Systems	
GCMS:	GCMS-TQ8040 NX
Autosampler:	AOC-6000 Plus
Column:	SH-PolarWax (60 m, 0.25 mm I.D., df = 0.25 µm) P/N: 227-36247-02
AOC-6000 Plus	
SPME Arrow:	O.D. 1.1 mm DVB/PDMS, 120 µm
Conditioning Temp.:	270 °C
Pre Conditioning Time:	10 min
Incubation Temp.:	40 °C
Incubation Time:	5 min
Stirrer Speed:	250 rpm
Agitator Speed:	250 rpm
Sample Extract Time:	35 min
Sample Desorb Time:	2 min
Post-Conditioning Time:	5 min
GC	
Injection Temperature:	250 °C
Injection Mode:	Split (Split Ratio 1)
Purge Flow:	3.0 mL/min
Carrier Gas Control:	Const. Liner Velocity (25.5 cm/sec)
Oven Temperature:	40 °C (5 min) → 3 °C/min → 150 °C → 25 °C/min → 250 °C (4.33 min)
MS	
Data Acquisition Mode:	MRM
Loop Time:	0.3 sec
Tuning Mode:	High Sensitivity
Interface Temp.:	250 °C
Ion Source Temp.:	200 °C
Solvent Cut Time:	3 min

Table 3 MRM Transitions for Target Analytes

	Quantitative *m/z*	Qualitative 1 *m/z*	Qualitative 2 *m/z*
MDMP	120.00 > 79.00	120.00 > 52.00	138.00 > 120.00
IPMP	152.00 > 137.00	137.00 > 109.00	152.00 > 124.00
IBMP	124.00 > 94.10	124.00 > 81.10	124.00 > 68.10
SBMP	138.00 > 123.10	138.00 > 119.10	151.10 > 123.10
EMP	138.00 > 123.10	138.00 > 81.00	123.00 > 95.00

■ Calibration and Performance in Matrix

A processed tomato product was diluted 4-fold with distilled water and spiked with the five target pyrazines to final concentrations of 5 – 50 ng/L. After spiking, NaCl was added and calibration curves were obtained.

Fig. 5 shows MRM chromatograms at the lowest calibration level (5 ng/L) and the corresponding calibration curves. All analytes showed good linearity (R^2 > 0.996). Repeatability was also good: at 10 ng/L, the peak area %RSD (n = 5) was ≤ 6 % for all analytes.

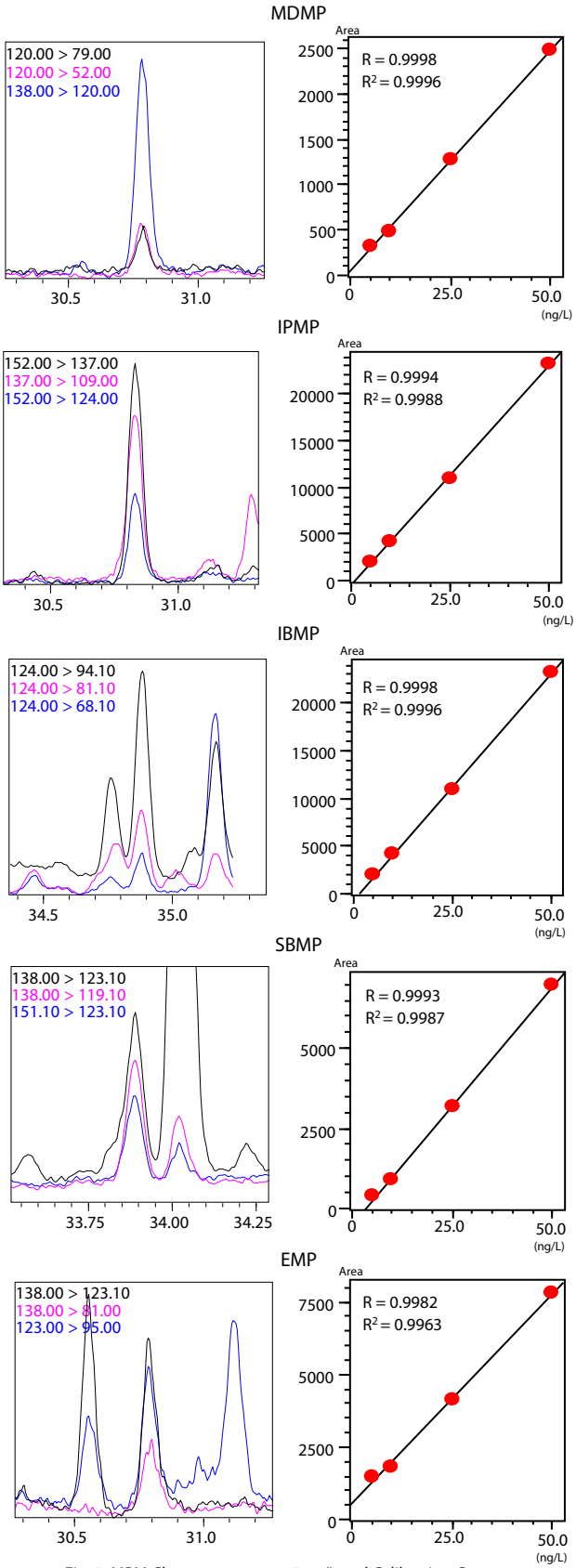


Fig. 5 MRM Chromatograms at 5 ng/L and Calibration Curves for Each Analyte

■ Quantitation of Real Samples

Four processed tomato product samples identified by sensory evaluation as having a vegetative off-flavor were analyzed (Table 4).

MDMP was detected in all four samples. Two samples were below the quantitation range and are reported as <LOQ. The MRM chromatogram for detected MDMP is shown in Fig. 6.

IPMP was detected in three of the four samples at <LOQ. The corresponding MRM chromatogram is shown in Fig. 7.

The remaining three methoxypyrazines were not detected in any of the samples.

Table 4 Quantitative Results for Each Analyte

	Quantitative Results (ng/L)			
	Sample 1	Sample 2	Sample 3	Sample 4
MDMP	21	53	< LOQ	< LOQ
IPMP	< LOQ	< LOQ	N.D.	< LOQ
IBMP	N.D.	N.D.	N.D.	N.D.
SBMP	N.D.	N.D.	N.D.	N.D.
EMP	N.D.	N.D.	N.D.	N.D.

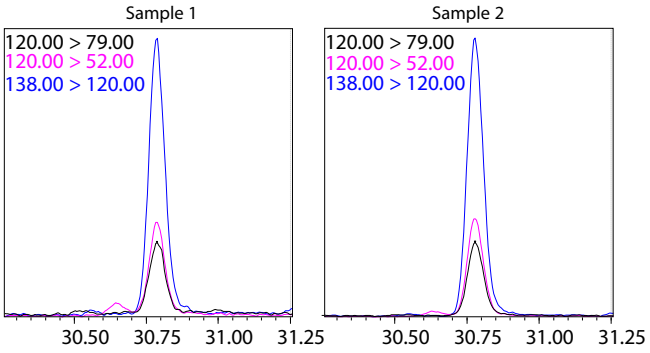


Fig. 6 MRM Chromatograms of MDMP in Samples 1 and 2

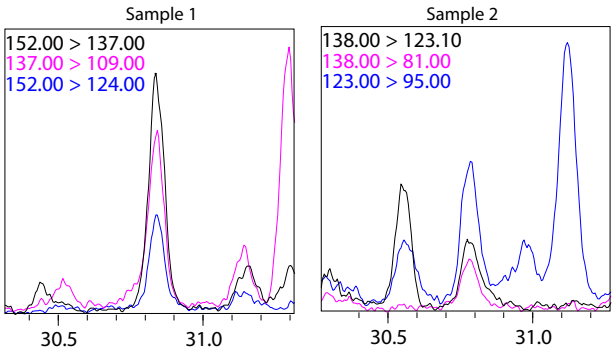


Fig. 7 MRM Chromatograms of IPMP in Samples 1 and 2

■ Conclusion

By using an AOC-6000 Plus autosampler with the GCMS-TQ8040 NX system and optimizing the SPME Arrow injection method, five off-flavor methoxypyrazines were successfully measured at ng/L (ppt) levels. Using MRM improved selectivity and enabled isomer-specific analysis, including differentiation of isomers that are difficult to separate by GC alone.

When applied to real processed tomato products, the method enabled quantitation of 2-methoxy-3,5-dimethylpyrazine (MDMP). This system reduces matrix interference and provides high sensitivity for trace-level off-flavor compounds.

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