Qualitative Analysis of Grated Daikon Radish by using HS-SPME-GC-QMS and msFineAnalysis iQ

Product used: Mass Spectrometer (MS)

Introduction

Food flavor components are known to be an important element of good taste, and off-flavor components, such as rancid odors, are also an important element of food quality. Gas chromatograph mass spectrometer (GC-MS) is often used to analyze these food flavor components due to the high volatility of flavor components and the complex composition of many components.

In qualitative analysis using GC-MS, compound identification is commonly performed by library search using commercially available electron ionization (EI) mass spectral database (DB) like NIST DB. However, if qualitative analysis is performed using only the similarity with the DB spectrum as an index, several significant candidates may be obtained depending on the compound, or erroneous candidates may be selected as the identification result. In such cases, confirmation of molecular ions by the soft ionization (SI) such as the photoionization (PI) is effective. In 2021, we released msFineAnalysis iQ, an integrated qualitative analysis software that automatically combines the analysis results of EI and SI methods measured by GC-QMS. msFineAnalysis iQ also has two sample comparison (differential analysis) function, which can extract characteristic and common components between samples. In this function, if data for EI is measured with n=3 or n=5, a difference analysis with statistical reproducibility can be performed. However, a difference analysis based on a simple intensity comparison can also be performed for n=1 data.

Therefore, in this MSTips, we report the comparison result of “grated daikon radish” and “diced daikon radish” (n=1 each) using msFineAnalysis iQ.

Experimental

Two types of daikon were used in the sample: grated daikon radish and diced daikon radish. A GC-QMS (JMS-Q1600GC UltraQuad™ SQ-Zeta, JEOL Ltd., Figure 1) was used for the measurement. The SPME mode of the HT2850T autosampler (HTA S.R.L.) was used as the sample pretreatment device, and volatile components in the headspace area of the vials were targeted for the measurement. We performed HS-SPME-GC-QMS measurements using both EI and photoionization (PI) modes with a combination EI/PI ion source. In this measurement, the EI and PI were measured at n=1 and n=1, respectively. The qualitative data processing was performed with msFineAnalysis iQ (JEOL Ltd.). Differential analysis was also performed with msFineAnalysis iQ using TICC of EI data. Detailed measurement conditions are shown in Table 1.

Figure 1 JMS-Q1600GC with HT2850T autosampler

Table 1 Measurement conditions

SPME	
SPME Fiber	DVB/CAR/PDMS 2mm (Merck)
Sample amount	5 g
Extraction temp.	50 °C
Extraction time	30 min
Desorption time	3 min
GC	
Column	ZB-WAX (Phenomenex) 30 m×0.25 mm I.D., df=0.25 µm
Inlet	300℃, EI=Split 20:1, PI=Splitless
Oven	40℃ (2 min) →10℃/min→250℃/min (5min)
Carrier flow	He, 1.0 mL/min (Constant Flow)
MS	
Ion Source	EI/PI combination ion source
Ionization mode	EI+ (70 eV, 50 µA), PI+ (D2 lamp, 8～10 eV)
Mass range	*m/z* 33-500 (Scan mode)

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Results and Discussion

Figure 2 shows TICC of EI data: Blue is grated daikon radish, Red is diced daikon radish. The grated daikon radish data had more peaks. Table 2 shows integrated analysis results of grated daikon radish data. These results showed that many isocyanates (-N=C=S) and sulfur-containing compounds were detected by grated daikon radish. Mass spectra of ID: 020 are shown Figure 3. This compound was estimated "trans-Raphasatin" by integrated analysis result in Table 2, and its molecular ion was detected in PI. And isotope pattern matching result between observed and calculated of ID: 020 is shown Figure 4. In the isotope patterns of compounds containing sulfur, the relative intensity of [M+2] is high, and a similar trend was observed in the results of this measurement. The agreement score between observed and calculated values was 0.99 (Max 1.00), which was very good.

The spicy flavor compounds in daikon radish are known to come mainly from isocyanates. It is also known that isocyanates in daikon radish are produced by cell breakdown when grated, and the compounds detected in the grated daikon radish in this study supported the above.

These results show that the differential analysis function of msFineAnalysis iQ can easily extract and qualify compounds characteristic of grated daikon radish.

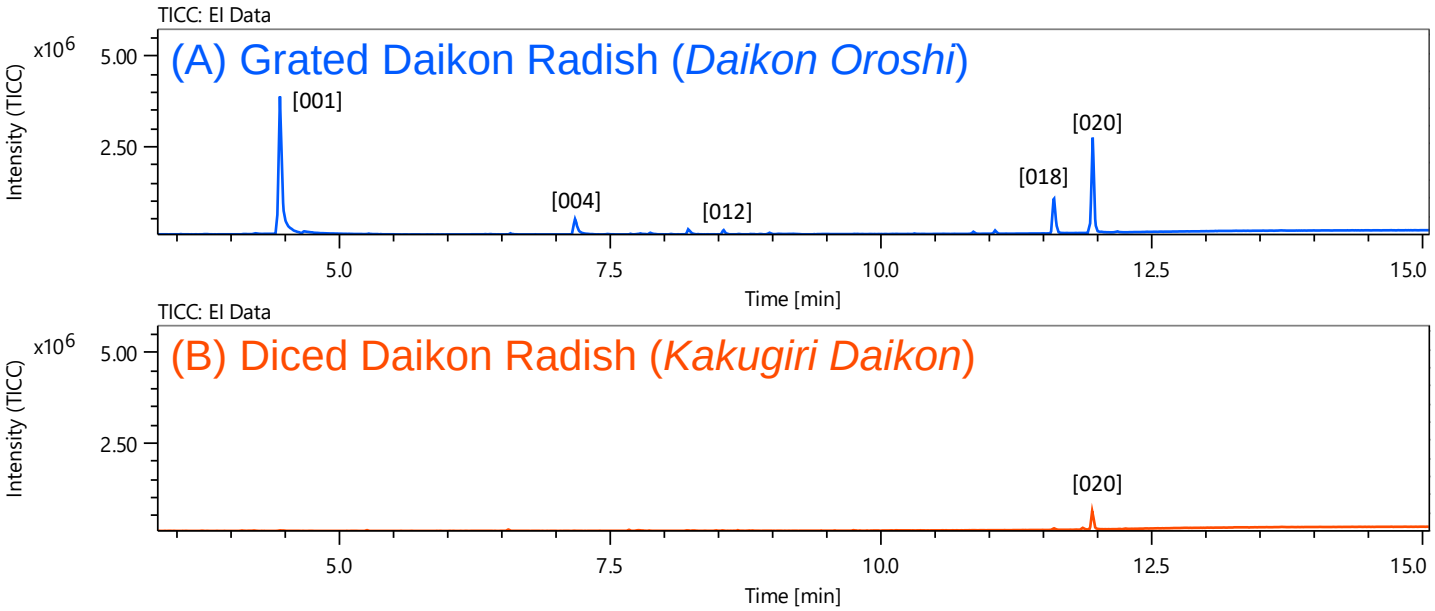

Figure 2 Total ion current chromatograms of EI

Table 2 Characteristic compounds in grated daikon radish (*Daikon Oroshi*)

	General				Variance		Total Result										
	ID	RT [min]	RI [iu]	Height [%]	Class	Log2(B/A)	Library Name	CAS#	Lib.	Similarity	Lib. RI [iu]	ΔRI [iu]	Formula	DBE	EI Base Peak (Lib.)	MW	Isotope Matching
	001	4.45	1078	100.00	A > B	< -4	Disulfide, dimethyl	624-92-0	mainlib	976	1077	1	C2 H6 S2	0.0	94	94	0.98
★	020	11.96	2254	69.41	A > B	-2.41	trans-Raphasatin	13028-50-7	mainlib	970	N/A	N/A	C6 H9 N S2	3.0	87	159	0.99
	018	11.60	2177	25.53	A > B	< -4	1-Butene, 4-isothiocyanato-1-(methylthio)-	51598-96-0	mainlib	701	2129	48	C6 H9 N S2	3.0	87	159	0.35
	004	7.18	1403	11.15	A Only	< -4	Dimethyl trisulfide	3658-80-8	mainlib	964	1377	26	C2 H6 S3	0.0	126	126	0.95
	010	8.22	1559	3.65	A Only	< -4	Hexane, 1-isothiocyanato-	4404-45-9	mainlib	756	1582	23	C7 H13 N S	2.0	43	143	0.73
	012	8.55	1610	3.08	A Only	< -4	Hexane, 1-isothiocyanato-	4404-45-9	mainlib	864	1582	28	C7 H13 N S	2.0	43	143	N/A
	017	11.06	2064	2.43	A Only	< -4	cis-Raphasatin	123954-93-8	mainlib	665	N/A	N/A	C6 H9 N S2	3.0	87	159	-
	016	10.86	2024	1.53	A Only	< -4	Propane, 1-isothiocyanato-3-(methylthio)-	505-79-3	mainlib	936	1975	49	C5 H9 N S2	2.0	101	147	N/A
	008	7.87	1504	1.16	A Only	< -4	n-Pentyl isothiocyanate	629-12-9	mainlib	744	1507	3	C6 H11 N S	2.0	43	129	0.75
	014	8.97	1681	1.09	A Only	< -4	4,8-Dioxaspiro[2.5]oct-1-ene, 6,6-dimethyl-	60935-22-0	mainlib	521	677-1261	420	C8 H12 O2	3.0	55	140	0.48

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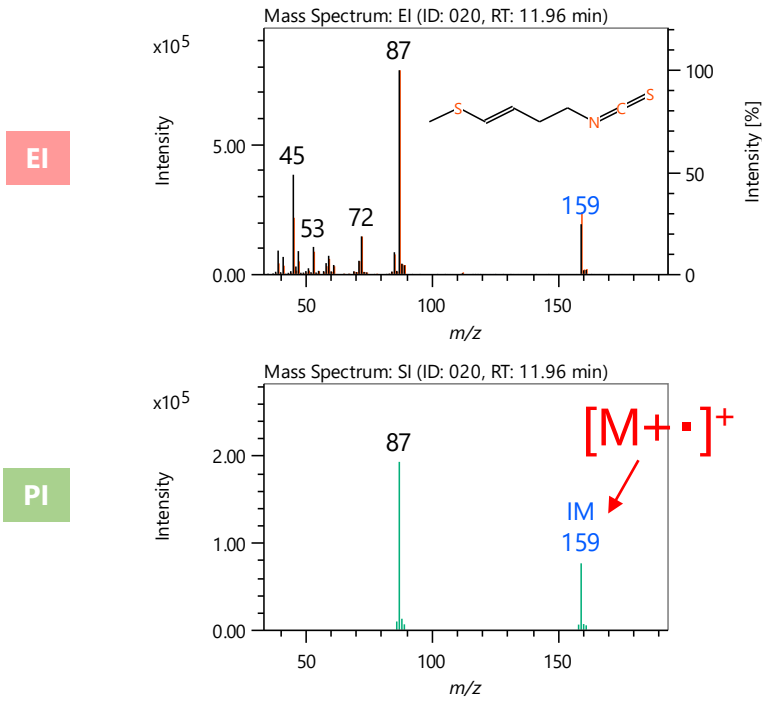
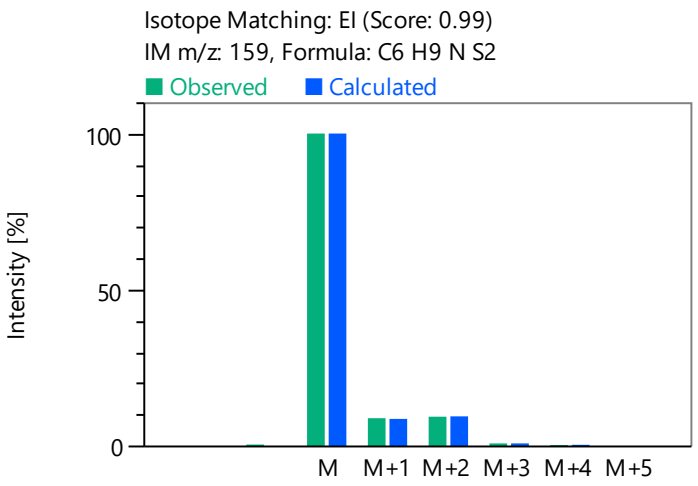


Figure 3 Mass spectra of ID: 020



m/z	Observed	Calculated
159 [M]	100.00	100.00
160 [M+1]	8.76	8.56
161 [M+2]	9.27	9.36
162 [M+3]	0.68	0.71
163 [M+4]	0.18	0.27
164 [M+5]	-	-
165 [M+6]	-	-
166 [M+7]	-	-
167 [M+8]	-	-
168 [M+9]	-	-

Figure 4 Isotope pattern matching results for ID: 020 molecular ion

Conclusions

In this MSTips, we reported the comparison results of grated and diced daikon radish using differential analysis function of msFineAnalysis iQ. This function allowed us to extract components unique to grated daikon radish and to consider the components that occur when daikon radish is grated.

This software is expected to improve the qualitative accuracy and efficiency of qualitative analysis in foods using GC-QMS.

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