Comparison of aromatic compounds in two different red wines by using GC–High resolution TOFMS with the integrated data analysis of msFineAnalysis AI

Related products: Mass Spectrometer (MS)

Introduction

It is known that the taste of alcoholic beverages such as wine has a strong influence from aromatic compounds. It is also known there are many common aromatic compounds that contribute to the typical taste and aromas of wine independent of the production regions, and there are also many aromatic compounds that are strongly dependent on the production regions and the kinds of grapes.

In case of wine, the difference of taste and aroma between the wines that were brewed the different production region is often discussed. It is of interest to know the type of aromatic compounds that contribute to those differences.

The combination of the micro solid-phase extraction (SPME) and gas chromatograph-mass spectrometer (GC-MS) is widely used for the analysis not only of aromatic compounds but also volatile organic compounds. The combined analysis method was used to detect the characteristic compounds of two type of red wines, Bordeaux and Bourgogne. All aromatic samples were measured by not only electron ionization (EI) but also photoionization (PI) to identify the characteristic chemical compounds that were included in the only Bordeaux or only Bourgogne wine. In addition, both measurement data were analyzed by using msFineAnalysis AI software. The characteristics chemical compounds that differ between the two wines were identified by using the differential analysis functionality of msFineAnalysis AI.

JMS-T2000GC AccuTOF™ GC-Alpha

Experiment

Two typical red wines, produced in Bordeaux and Bourgogne, which are generally available in a supermarkets were used as test samples. 2 mL portion of the wine samples were added to 15mL glass vial and immediately sealed. The SPME fiber was inserted into the headspace of the glass vial and the fiber was exposed for 20 min at room temperature. All extracted compounds in the SPME fiber were introduced into GC by heating at injection port of GC for 1min. The details of measurement condition were shown in Table 1. To use the differential analysis functionality, each sample was measured for three times using EI ionization. Then those measurement results were applied to msFineAnalysis AI (JEOL Ltd.) together with the measurement results by PI ionization.

Table 1. Measurement condition

GC Condtion	
GC	8890GC (Agilent)
Injection mode	Pulsed Splitless
	Purge Pressure : 100kPa
	Pulsed time : 1.0 min
	Purge Flow : 20mL/min
	Purge On time : 0.9 min
	Septum Purge Flow : 3.0 mL/min
Injection Temp	250°C
Column	InertCap WAX (GL Science)
	30m X 0.25mm(I.D.), 0.25µm Film Thickness
Oven	40°C (3 min) > 7°C/min > 90°C (0min)
	> 20°C/min > 240°C (7.36min)
He Flow	1mL/min (Constant Flow mode)

MS Condition	
Mass Spectrometer	JMS-T2000GC AccuTOF™ GC-Alpha
Ion source	EI/PI Combination Ion Source
Ionizetion	EI+ : 70eV, 300µA
	PI+ : D2 lamp, 115-400nm
Source tem.	250°C
GC Interface temp.	250°C
m/z range	m/z 40 - 550

SPME condition	
Fiber	50/30µm DVB/CAR/PDMS (Gray)
Sampling Method	Headspace
Sample Amaount	2mL
Extraction Temp	Room temperature
Extraction Time	20 min
Desorption time	1 min

Results

Total Ion Current Chromatograms (TICCs) obtained as a result of measuring the aromatic components of Bordeaux and Bourgogne wines by EI ionization are shown in Fig.1. In addition, the volcano plot obtained as a result of performing a difference analysis using Bordeaux wine as Sample A (blue) and Bourgogne wine as Sample B (red) is shown in Fig.2. In the volcano plot of msFineAnalysis AI software, the horizontal axis represents the intensity ratio between two samples (Log2(B/A)), and the vertical axis represents statistical reproducibility (-log10(p-value)). By using this volcano plot, it becomes easy to understand the difference in components. The plots in the area with a blue background shown in Fig. 2 are characteristically detected peaks in Sample A, and conversely, those with a red background are the characteristically peaks in Sample B.

JEOL Ltd.
3-1-2 Musashino Akishima Tokyo 196-8558 Japan Sales Division Tel. +81-3-6262-3560 Fax. +81-3-6262-3577
www.jeol.com ISO 9001 • ISO 14001 Certified

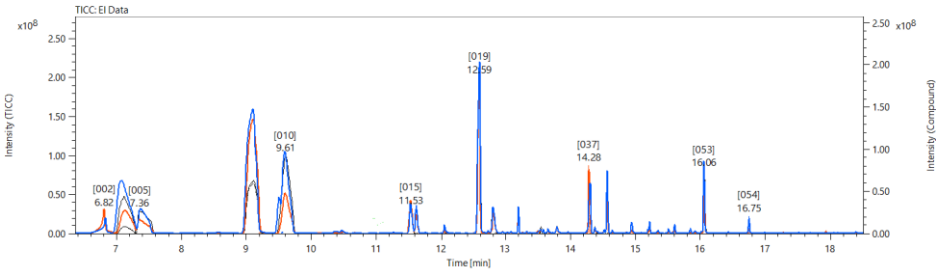

Fig.1 TICC with EI for Sample A(Blue) and B(Red)

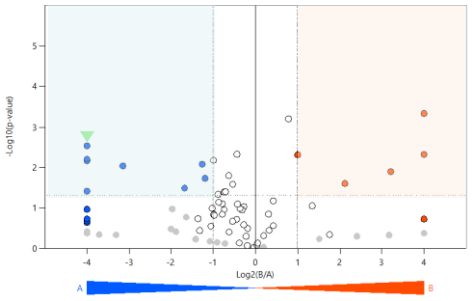

Fig.2 Volcano plot of Bordeaux(Blue) vs. Bourgogne(Red)

Table 2. Integrated qualitative analysis results for the characteristic compounds for Sample A (Bordeaux) and Sample B (Bourgogne)

Variance Component Analysis Result						Total Result						
RT [min]	Area	IM m/z	Class	Log2(B/A)	p-value	Compound Name	Similarity	Formula	Calculated m/z	Mass Error [mDa]	Isotope Matching	EI Fragment Coverage
Characteristic Compounds for Sample A												
5.36	59432816	116.08281	A Only	< -4	0.007	Butanoic acid, ethyl ester	731	C6 H12 O2	116.08318	-0.37	0.89	100
10.37	14756626	-	A Only	< -4	0.006	Acetic acid, hexyl ester	909	C8 H16 O2	-	-	-	100
11.07	2354736	-	A Only	< -4	0.003	1-Pentene, 4-methyl-	810	C6 H12	84.09335	-0.72	N/A	100
11.26	3623007	84.09313	A > B	-1.68	0.033	Cyclopropane, propyl-	746	C6 H12	84.09335	-0.22	N/A	100
13.96	2992587	-	A Only	< -4	0.109	Propylene Glycol	840	C3 H8 O2	76.05188	-0.53	0.61	100
15.35	5287901	152.04676	A Only	< -4	0.039	Methyl salicylate	763	C8 H8 O3	152.04680	-0.04	0.91	88
15.61	16329082	-	A > B	-1.26	0.008	Hexanoic acid	865	C6 H12 O2	117.09101	-0.82	N/A	100
15.85	9603910	108.05672	A > B	-3.15	0.009	Benzyl alcohol	942	C7 H8 O	108.05697	-0.24	0.89	100
16.74	27620411	144.11423	A > B	-1.19	0.019	Octanoic acid	949	C8 H16 O2	144.11448	-0.25	0.63	100
Characteristic Compounds for Sample B												
13.27	2658553	-	A < B	3.21	0.013	(S)-3-Ethyl-4-methylpentanol	931	C8 H18 O	-	-	-	100
13.50	5535502	192.15035	B Only	> 4	0.000	2(1H)-Naphthalenone, 3,4,4a,5,6,7-hexahydro-1,1,4a-trimethyl-	751	C13 H20 O	192.15087	-0.52	0.81	90
14.28	110243250	200.17694	A < B	1.00	0.005	Decanoic acid, ethyl ester	921	C12 H24 O2	200.17708	-0.15	0.70	95
15.57	2263498	-	B Only	> 4	0.005	Dodecanoic acid, ethyl ester	865	C14 H28 O2	228.20838	0.17	0.81	100
17.93	4687977	206.16637	A < B	2.13	0.025	2,4-Di-tert-butylphenol	945	C14 H22 O	206.16652	-0.14	0.89	100

The characteristic compounds in each sample (Bordeaux : Sample A and Bourgogne : Sample B) were identified and listed in Table 2. Totally 14 compounds (9 from Bordeaux, 5 from Bourgogne) were identified. Concerning 8 of 14 compounds, the molecular ions were identified, and the exact m/z values of those molecular ions agreed with the exact m/z values of the estimated compounds. In addition, the EI fragment coverage values for those compounds that are calculated from the relationship between the elemental composition of fragment ions and those of molecular ion were also high values. This means the validity of the compound identification is much higher than by simple library search alone.

It is known that several 'carboxylic acid esters' are the typical aromatic compounds that characterized the aroma of wine. Many kinds of methyl and/or ethyl esters of low fatty acids were detected from both of Bordeaux and Bourgogne wine. This means that the esters of low fatty acids strongly contribute the aroma of wines.

The comparison of TICC by EI and PI for Hexanoic acid ethyl ester that was detected from both of Bordeaux and Bourgogne wines is shown in Fig 3. The position of the Hexanoic acid ethyl ester in the volcano plot is also shown in Fig.4. By using the differential analysis functionality of msFineAnalysis, the detailed data analysis and confirming information is available for each peak.

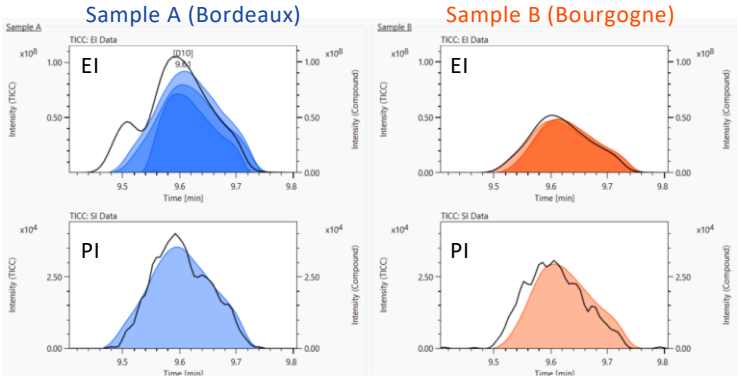

Fig.3 TICC of EI and PI for Hexanoic acid ethyl ester detected in Sample A and Sample B

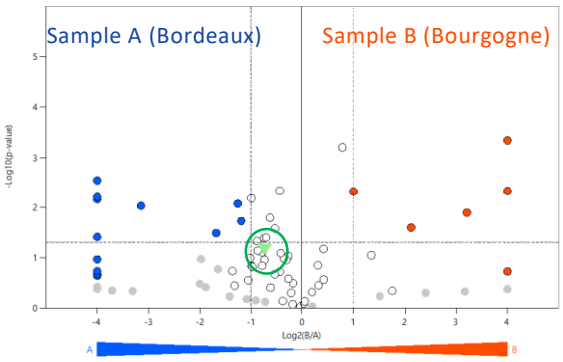

Fig.4 Relative position of Hexanoic acid ethyl ester in Volcano plot

JEOL Ltd.
3-1-2 Musashino Akishima Tokyo 196-8558 Japan Sales Division Tel. +81-3-6262-3560 Fax. +81-3-6262-3577
www.jeol.com ISO 9001・ISO 14001 Certified

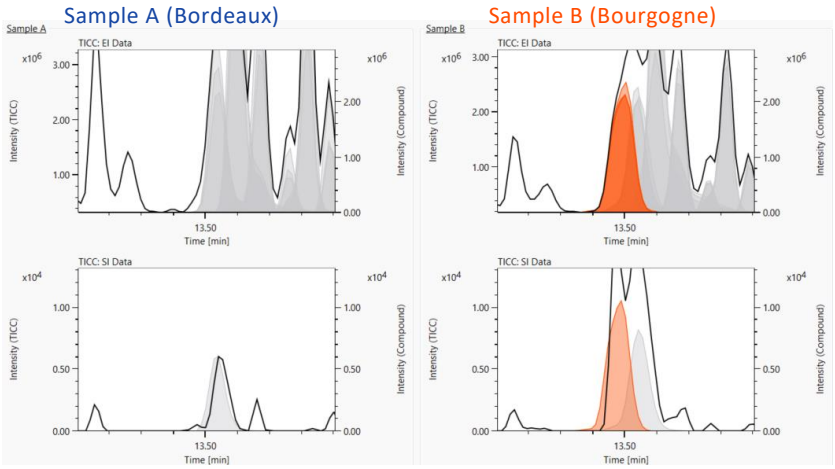

Fig.5 TICC of EI and PI for 3,4,4a,5,6,7-hexahydro-1,1,4a-trimethyl-2(1H)-Naphthalenone detected only in Sample B (not in Sample A)

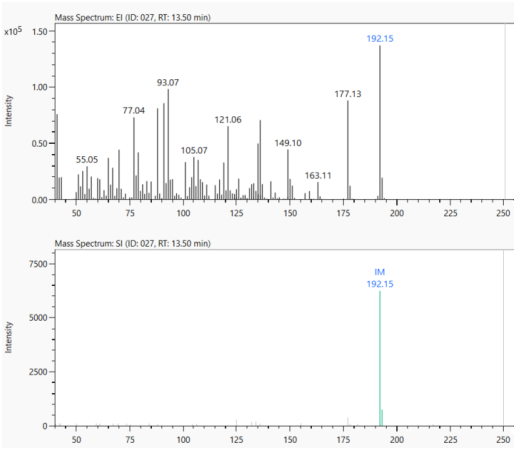

Fig.6 Mass spectrum of 3,4,4a,5,6,7-hexahydro-1,1,4a-trimethyl-2(1H)-Naphthalenone detected in Sample B

It is interesting to note that esters of fatty acids with a relatively large number of carbon atoms were detected as the characteristic compounds of Bourgogne wine.
Several compounds such as Propylene Glycol and Methyl salicylate in Bordeaux wines and 3,4,4a,5,6,7-hexahydro-1,1,4a-trimethyl-2(1H)-Naphthalenone in Bourgogne wines were detected as characteristic compounds for only one of the two types of wine.
The TICC's of EI and PI measurements for 3,4,4a,5,6,7-hexahydro-1,1,4a-trimethyl-2(1H)-Naphthalenone is shown in Fig.5. Although the peak corresponding to 3,4,4a,5,6,7-hexahydro-1,1,4a-trimethyl-2(1H)-Naphthalenone was detected as a shoulder peak beside of a huge peak, it was clearly detected using the chromatographic deconvolution functionality of msFineAnalysis AI. The mass spectra of 3,4,4a,5,6,7-hexahydro-1,1,4a-trimethyl-2(1H)-Naphthalenone measured by EI and PI is shown Fig. 6.

In total 14 compounds were found as characteristic compounds from only Bordeaux and only Bourgogne wine in this study. It is suggested that those compounds contribute the characteristic aroma and taste for both wines.

Conclusion

In this MSTips, we introduced an example of difference analysis by using msFineAnalysis AI concerning aroma components in wines from different production areas.

By using msFineAnalysis AI, qualitative analysis for GC-TOFMS is expected to be more accurate and efficient.

JEOL Ltd.
3-1-2 Musashino Akishima Tokyo 196-8558 Japan Sales Division Tel. +81-3-6262-3560 Fax. +81-3-6262-3577
www.jeol.com ISO 9001 • ISO 14001 Certified