Differential analysis in two different types of water-based ink products using msFineAnalysis iQ

Product used：Mass Spectrometer (MS)

Introduction

Usually, qualitative analysis by GC-QMS is generally performed by library database (DB) search in the measurement data of electron ionization (EI) method. However, when qualitative analysis is performed using only the similarity index with the library spectrum, a plurality of significant candidates may be obtained depending on the compound, or an erroneous candidate may be selected as the identification result. Therefore, it is effective to confirm molecular ions by soft ionization (SI) method including photoionization (PI) method.

In this case, two types of measurement data, the EI method and the SI method, are obtained for a single sample, making data analysis more complicated. Therefore, an integrated qualitative analysis software that can quickly and automatically analyze the two types of data is desired. This is the reason why we have developed msFineAnalysis iQ.

In our previous report, MSTips No. 395, we reported an example of integrated qualitative analysis using msFineAnalysis iQ for major constituents in water-based ink. Furthermore, in this report, we report an example of difference analysis in two different types of water-based ink products.

Experimental

Two water-based inks for inkjet printers, magenta and cyan, were used as samples. A GC-QMS (JMS-Q1600GC UltraQuad™ SQ-Zeta, manufactured by JEOL Ltd.) was used for the measurement. 1 µL of the undiluted sample was injected into the GC, and the EI method and the PI method were used as ionization methods. Table 1 shows the detailed measurement conditions. Analysis was performed using the difference analysis function of msFineAnalysis iQ (manufactured by JEOL Ltd.), an integrated qualitative analysis software dedicated to GC-QMS.

JMS-Q1600GC UltraQuad™ SQ-Zeta

Table 1 Measurement condition

GC	
Column	VF-5MS (Agilent Technologies) 30 m×0.25 mm I.D., df=0.25 µm
Injecter Temp.	320℃
Oven Temp.	40℃(1min)→ 10℃/min → 320℃ (3min)
Injection Mode	Split 200:1
Carrier Gas	He, 1.0 ml/min (Constant Flow)

MS	
Ionization Temp.	250℃
Interface Temp.	280℃
Ion Source	EI/PI Conbination Ion Source
Ionization Mode	EI (70 eV, 50 µA), PI (8～10 eV)
mode	Scan (*m/z* 15 - 600)

Result and Discussion

Figure 1 shows the GC/MS measurement results of water-based inks (magenta and cyan). The upper row is the total ion current chromatogram (TICC) of magenta and the lower row of cyan. For both aqueous inks, the two peaks with early elution times were presumed to be water as solvent and isopropyl alcohol (IPA) as penetrant. In addition, the broad peak detected around 9 minutes retention time was glycerin as a drying inhibitor. And then, ``Surfynol 104'', a type of surfactant intended for wetting/penetrating, foaming/defoaming functions in water-based ink, was also detected.

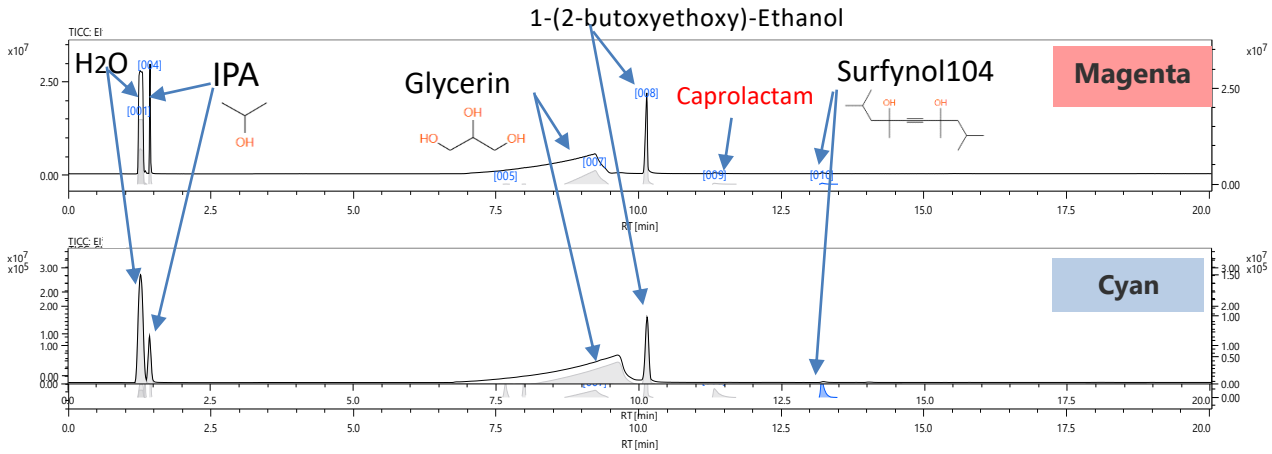

Figure 1 Total ion current chromatograms

Figure 2 shows TICC enlargements and volcano plots for retention times from 5 to 13 minutes obtained by the difference analysis function of msFineAnalysis iQ. A number of minute peaks were detected overlapping with the broad peak of glycerol at a retention time of around 9 minutes. Table 2 shows the integrated analysis result list. From these results, 11 kinds of compounds were qualitatively obtained through both samples.

A volcano plot is a scatter plot that can visualize characteristic compounds between samples, with the intensity ratio (Log2(B/A)) on the horizontal axis and the statistical reproducibility (-Log10(p-value) on the vertical axis) respectively. This time, the left area of the volcano plot shows the compounds specifically included in cyan and the right area in magenta. The compounds specifically contained in each sample were caprolactam for magenta, and four compounds for cyan, including ID: 005 "Ethanol, 2,2'-oxybis- (diethylene glycol)".

Figure 3 shows the mass spectrum of the peak of [ID:007]. An ion of m/z 121, presumed to be a molecular ion, could be detected on both EI and PI mass spectra. Table 3 shows the integrated analysis result list (top 5 candidates) by msFineAnalysis iQ. From this result, the peak [ID:007] was presumed to be "Benzenamine, N-ethyl- ". This compound was presumed to be a kind of solvent contained in water-based ink.

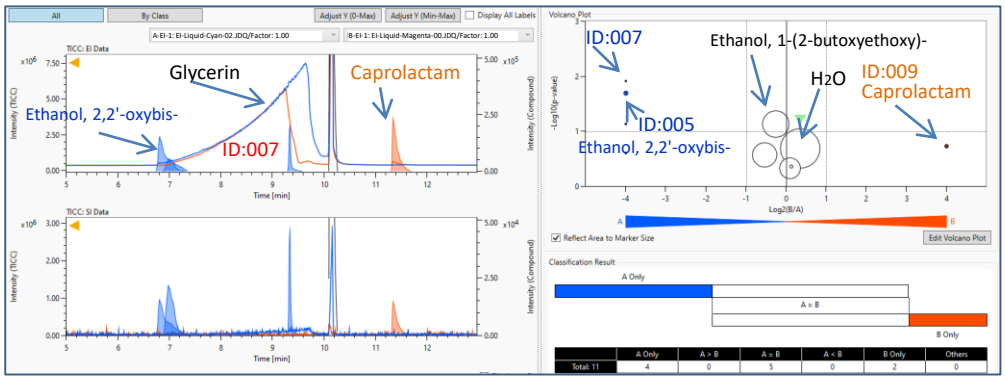

Figure 2 Volcano plot of variance compound analysis result

Table 2 Integrated qualitative analysis result of peak

Chromatogram information						Difference analysis result			Integrated analysis result							
ID	RT [min]	RI [iu]	Area	Height	Height [%]	Type	Log2(B/A)	p-value	Compound	CAS#	Similarity	Lib. RI [iu]	ΔRI [iu]	Fomula	Mw	Isotope Matching
001	1.23	645	57.66	22234643	77.67	A = B	0.35	0.202	Water	7732-18-5	904	317	329	H2 O	18	0.99
002	1.30	650	22.43	11165988	39.01	A = B	-0.54	0.265	Ammonia	7664-41-7	749	N/A	N/A	H3 N	17	N/A
003	1.36	653	0.22	1070288	3.74	B Only	> 4	0.184	Ethanol	64-17-5	920	427	226	C2 H6 O	46	0.83
004	1.43	658	16.47	28626418	100.00	A = B	0.10	0.463	Isopropyl Alcohol	67-63-0	953	489	169	C3 H8 O	60	0.99
005	6.82	984	0.82	153743	0.54	A Only	< -4	0.020	Ethanol, 2,2'-oxybis-	111-46-6	934	927	57	C4 H10 O3	106	0.33
006	6.95	992	0.24	52891	0.18	A Only	< -4	0.246	Aniline	62-53-3	832	977	17	C6 H7 N	93	0.85
007	9.33	1135	0.22	197769	0.69	A Only	< -4	0.012	Benzenamine, N-ethyl-	103-69-5	962	1128	8	C8 H11 N	121	0.97
008	10.16	1189	26.42	24601179	85.94	A = B	-0.26	0.073	Ethanol, 1-(2-butoxyethoxy)-	54446-78-5	953	1187	2	C8 H18 O3	162	-
009 ★	11.34	1270	0.67	236129	0.82	B Only	> 4	0.184	Caprolactam	105-60-2	955	1253	17	C6 H11 N O	113	0.93
010	13.23	1408	0.50	273662	0.96	A = B	0.13	0.431	2,4,7,9-Tetramethyl-5-decyn-4,7-diol	126-86-3	949	1407	1	C14 H26 O2	226	-
011	14.01	1469	0.28	106402	0.37	A Only	< -4	0.072	Ethanol, 2-[2-(2-butoxyethoxy)ethoxy]-	143-22-6	938	1486	17	C10 H22 O4	206	-

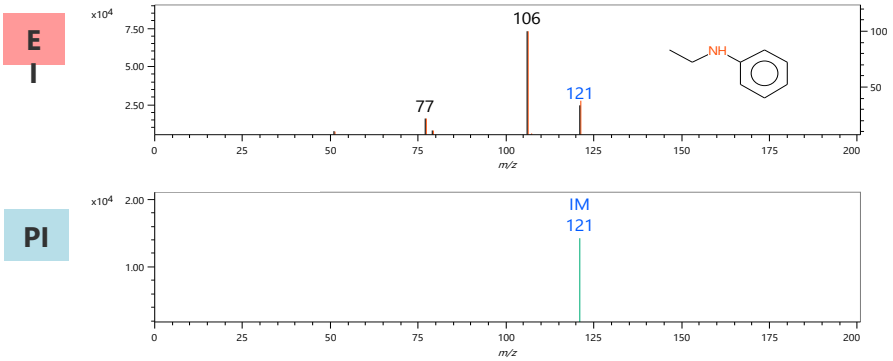

Figure 3 Mass spectra of peak [007]

Table 3 Integrated qualitative analysis result of peak [007]

	#	Compound	CAS#	Similarity	Similarity Reverse	Lib. RI [iu]	ΔRI [iu]	Formula	EI Base Peak (Lib.)	Mw	Mw confirmation	Isotope Matching
★	L01	Benzenamine, N-ethyl-	103-69-5	962	962	1128	8	C8 H11 N	106	121	?	0.97
	L02	Benzenamine, 2-ethyl-	578-54-1	870	870	1122	14	C8 H11 N	106	121	?	0.97
	L07	m-Ethylaniline	587-02-0	803	803	1141	5	C8 H11 N	106	121	?	0.97
	L09	Pyridine, 3-ethyl-5-methyl-	3999-78-8	794	795	645-1355	0	C8 H11 N	106	121	?	0.97
	L11	2,6-Xylidine	87-62-7	749	749	1168	32	C8 H11 N	121	121	?	0.97

Conclusion

In this report, we reported an example of difference analysis by msFineAnalysis iQ for major constituents in two colors (cyan and magenta) of water-based inks. msFineAnalysis iQ uses not only library DB search but also multiple identification functions such as retention index and isotope matching, so highly accurate qualitative analysis is possible. This software is expected to improve qualitative accuracy and efficient analysis work in GC-QMS analysis.

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
▼ Local office
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