Analysis of additives in polypropylene products using thermal desorption–GC–MS

Product used: Mass Spectrometer (MS)

Introduction

Thermal desorption (TD) is a GC pretreatment device for introducing gas samples such as atmospheric air and indoor air. It can also be used for gases generated from solid or liquid samples. In this MSTips, we introduce the analysis of additives in polypropylene products as the application of TD-GC-MS to material analysis. Figure 1 shows an overview of TD operation for measuring generated gas from a solid sample. ① Sampling: Seal the sample into an empty sample tube. If necessary, add the glass wool to fix the sample. ②Tube desorption: The sample tube is heated in the TD device, and the desorbed gas is collected in a cooled focusing trap. ③ Trap desorption: The focusing trap is heated at high speed and the desorbed gas is introduced into the GC in a narrow band width.

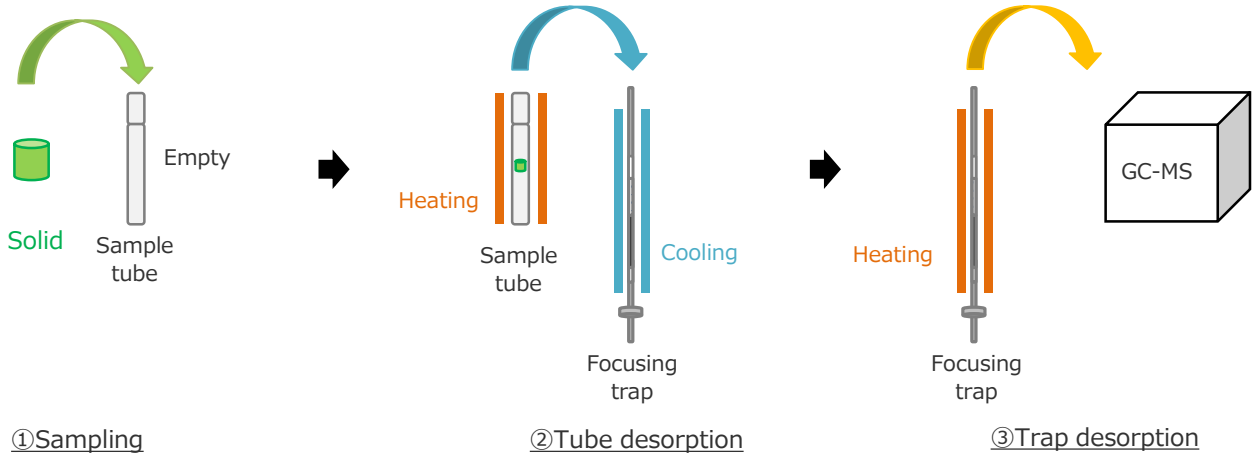


Figure 1 Overview of TD operation

Experiment

Two types of commercially available polypropylene films (Samples A and B), 30 mg each, were used as samples. Since the analysis target was additives, the tube desorption was set at a relatively low 90 °C for 30 minutes. msFineAnalysis iQ (JEOL) was used for analysis, and its differential analysis function extracted characteristic additives from each sample. Table 1 shows the measurement conditions of TD-GC-MS.

Table 1 Measurement conditions

TD conditions	
Thermal Desorption	TD-100xr (Markes International Ltd)
Sample tube type	Empty
Tube desorption	90°C (30min), 84mL/min, Splitless
Focusing trap type	General purpose Graphitized carbon (T11)
Trap cooling	-30 °C
Trap desorption	280°C (3min), 46mL/min, Split 22:1
Flow path temperature	240 °C

GC conditions	
Gas Chromatograph	8890A GC (Agilent Technologies)
Column	HP-5MS (Agilent Technologies) 30m x 0.25mm, 0.25µm
Oven Temperature	40°C(3min)-10°C/min -320°C(6min)
Carrier flow	He, 2.0mL/min

MS conditions	
Spectrometer	JMS-Q1600GC (JEOL Ltd.)
Ionization	EI+:70eV, 50µA
Ion source temperature	250 °C
Mass range	Scan, *m/z* 35-600

Results

Figure 2 shows the TIC chromatogram. Samples A and B were made of the same polypropylene, but there were significant differences in the detected peaks.

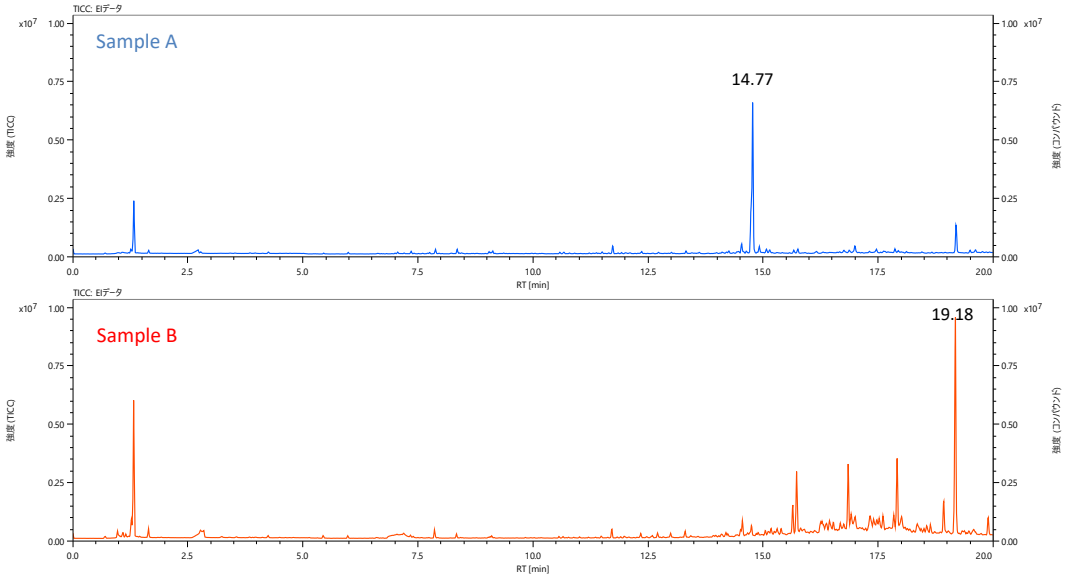
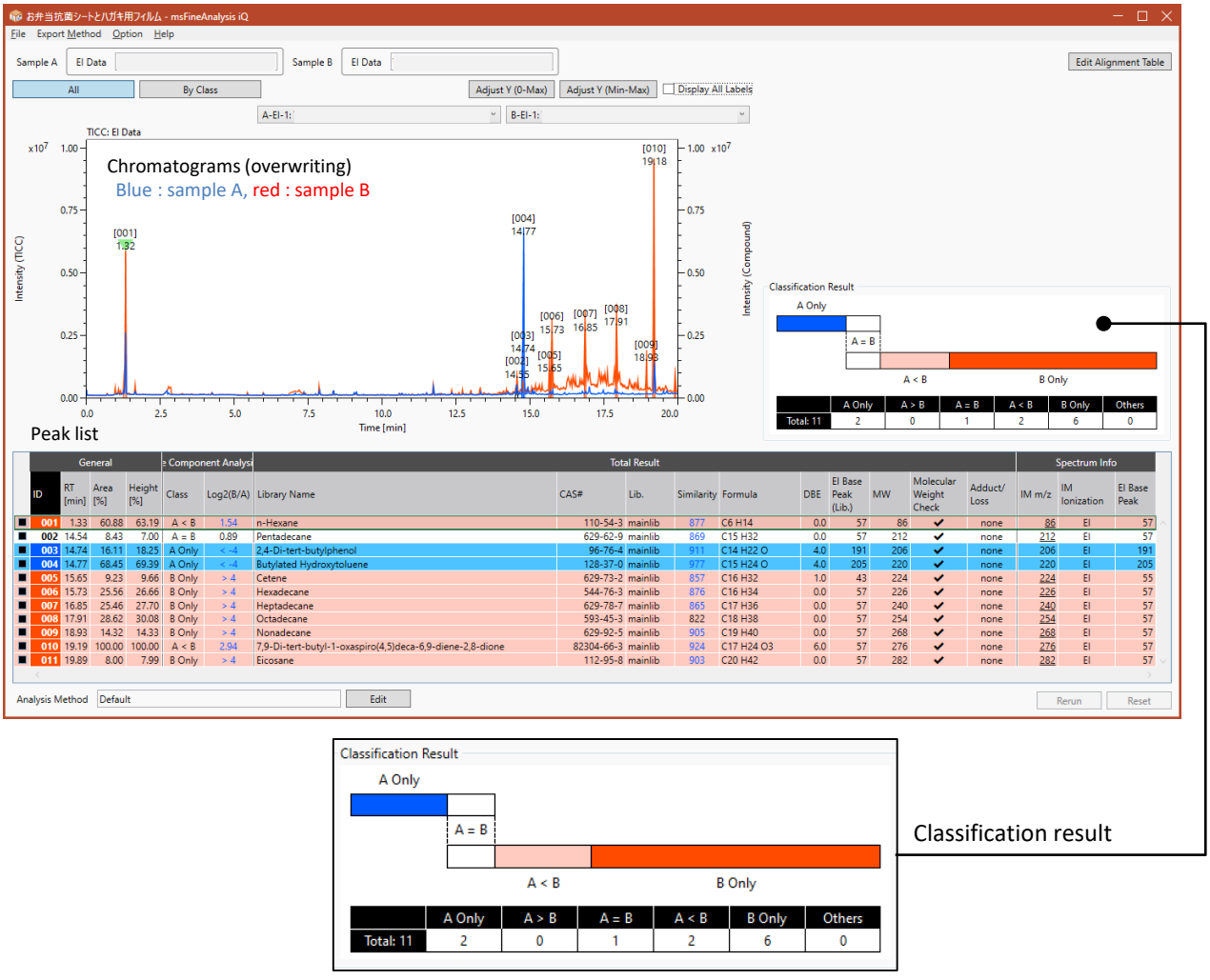


Figure 2 TIC chromatograms

Figure 3 shows the difference analysis results of msFineAnalysis iQ. From the 11 peaks with an intensity ratio of 5% or more to the maximum peak, 2 peaks that were strong in sample A and 8 peaks that were strong in sample B were extracted.



ID	RT [min]	Area [%]	Height [%]	Class	Log2(B/A)	Library Name	CAS#	Lib.	Similarity	Formula	DBE	EI Base Peak (Lib.)	MW	Molecular Weight Check	Adduct/ Loss	IM m/z	IM Ionization	EI Base Peak
001	1.33	60.88	63.19	A < B	1.54	n-Hexane	110-54-3	mainlib	877	C6 H14	0.0	57	86	✔	none	86	EI	57
002	14.54	8.43	7.00	A = B	0.89	Pentadecane	629-62-9	mainlib	869	C15 H32	0.0	57	212	✔	none	212	EI	57
003	14.74	16.11	18.25	A Only	< -4	2,4-Di-tert-butylphenol	96-76-4	mainlib	911	C14 H22 O	4.0	191	206	✔	none	206	EI	191
004	14.77	68.45	69.39	A Only	< -4	Butylated Hydroxytoluene	128-37-0	mainlib	977	C15 H24 O	4.0	205	220	✔	none	220	EI	205
005	15.65	9.23	9.66	B Only	> 4	Cetene	629-73-2	mainlib	857	C16 H32	1.0	43	224	✔	none	224	EI	55
006	15.73	25.56	26.66	B Only	> 4	Hexadecane	544-76-3	mainlib	876	C16 H34	0.0	57	226	✔	none	226	EI	57
007	16.85	25.46	27.70	B Only	> 4	Heptadecane	629-78-7	mainlib	865	C17 H36	0.0	57	240	✔	none	240	EI	57
008	17.91	28.62	30.08	B Only	> 4	Octadecane	593-45-3	mainlib	822	C18 H38	0.0	57	254	✔	none	254	EI	57
009	18.93	14.32	14.33	B Only	> 4	Nonadecane	629-92-5	mainlib	905	C19 H40	0.0	57	268	✔	none	268	EI	57
010	19.19	100.00	100.00	A < B	2.94	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	82304-66-3	mainlib	924	C17 H24 O3	6.0	57	276	✔	none	276	EI	57
011	19.89	8.00	7.99	B Only	> 4	Eicosane	112-95-8	mainlib	903	C20 H42	0.0	57	282	✔	none	282	EI	57

	A Only	A > B	A = B	A < B	B Only	Others
Total: 11	2	0	1	2	6	0

Figure 3 Difference analysis result of msFineAnalysis iQ

Table 2 shows the peak list of the qualitative analysis results. The background color indicates the intensity difference between samples. Blue is strong in sample A, red is strong in sample B, and white is not different between samples. In Addition, to improve the accuracy of qualitative analysis, msFineAnalysis iQ searches for molecular ions from measured mass spectra. In this result, it was possible to confirm molecular ions in all 11 peaks.

Table 2 Peak list of qualitative analysis result

General			Variance Component Analysis Result		Total Result								Spectrum Info
ID	RT [min]	Height [%]	Class	Log2(B/A)	Library Name	CAS#	Lib.	Similarity	Formula	DBE	MW	Molecular Weight Check	IM m/z
001	1.33	63.19	A < B	1.54	n-Hexane	110-54-3	mainlib	877	C6 H14	0.0	86	✔	86
002	14.54	7.00	A = B	0.89	Pentadecane	629-62-9	mainlib	869	C15 H32	0.0	212	✔	212
003	14.74	18.25	A Only	< -4	2,4-Di-tert-butylphenol	96-76-4	mainlib	911	C14 H22 O	4.0	206	✔	206
004	14.77	69.39	A Only	< -4	Butylated Hydroxytoluene	128-37-0	mainlib	977	C15 H24 O	4.0	220	✔	220
005	15.65	9.66	B Only	> 4	Cetene	629-73-2	mainlib	857	C16 H32	1.0	224	✔	224
006	15.73	26.66	B Only	> 4	Hexadecane	544-76-3	mainlib	876	C16 H34	0.0	226	✔	226
007	16.85	27.70	B Only	> 4	Heptadecane	629-78-7	mainlib	865	C17 H36	0.0	240	✔	240
008	17.91	30.08	B Only	> 4	Octadecane	593-45-3	mainlib	822	C18 H38	0.0	254	✔	254
009	18.93	14.33	B Only	> 4	Nonadecane	629-92-5	mainlib	905	C19 H40	0.0	268	✔	268
010	19.19	100.00	A < B	2.94	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	82304-66-3	mainlib	924	C17 H24 O3	6.0	276	✔	276
011	19.89	7.99	B Only	> 4	Eicosane	112-95-8	mainlib	903	C20 H42	0.0	282	✔	282

Checked when molecular ion is detected

Figure 4 shows the mass spectra of ID004 (detected at 14.77 min in sample A) and ID010 (detected at 19.19 min in sample B). As a result of qualitative analysis, the former was a phenolic antioxidant Butylated hydroxytoluene (BHT). The latter was [7,9-Di-tert-butyl- 1-oxaspiro(4,5)deca-6,9-diene-2,8-dione], which is a decomposition product of a hindered phenolic antioxidant Pentaerythritol tetrakis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate].

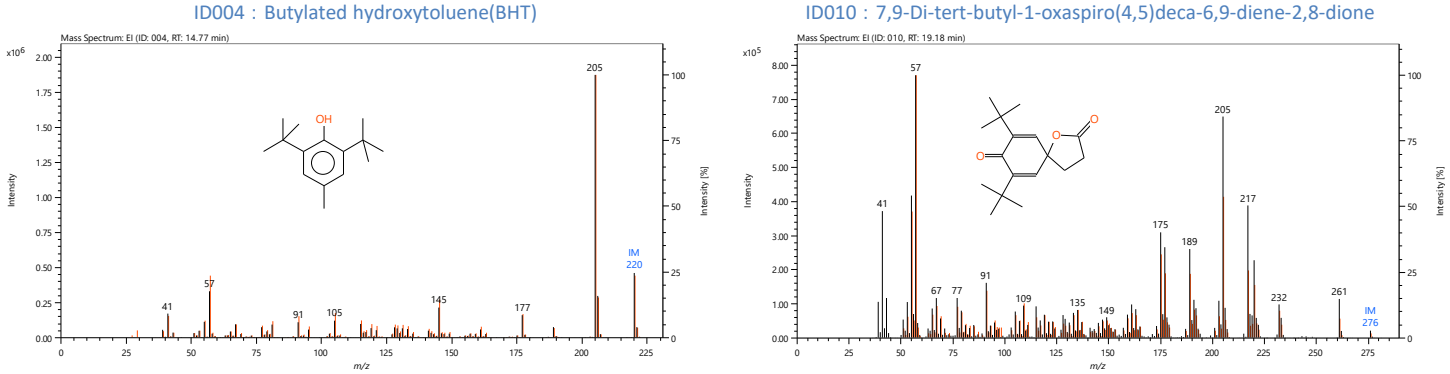


Figure 4 Mass spectra of ID004 and ID010

Conclusion

Using TD-100xr and JMS-Q1600GC, it is possible to analyze additives in propylene products with high sensitivity. In addition, msFineAnalysis iQ can easily extract characteristic components from complex chromatograms and perform qualitative analysis with high accuracy. These devices and software are also expected to be useful in materials 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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