Analysis of recycled PET products by Pyrolysis-GC-TOFMS

Product used: Mass Spectrometer (MS)

Introduction

The Circular economy is a global initiative that aims to realize a sustainable society by reducing the consumption of natural resources and maximizing the use of existing resources. Polymer (plastic) recycling is an important technology for achieving this. For example, many PET (polyethylene terephthalate) bottles are reused as PET bottles through horizontal recycling, but some are used for different products through cascade recycling (=downcycling). In addition, upcycling to use them in higher value products is also actively carried out. In these recycling process, evaluation of materials and products is important for stable quality, and Pyrolysis-GC-MS is commonly used as an analytical method.

In this MSTips, we will introduce an application of recycled PET products analysis using the high-performance gas chromatograph time-of-flight mass spectrometer "JMS-T2000GC" and unknown compounds structure analysis software "msFineAnalysis AI".

Experiment

As the sample, standard PET bottle and commercially available recycled PET product (buffer sheet) were used. 0.2 mg of each was weighed and measured using Pyrolysis-GC-MS. EI and FI (field ionization) methods were used for ionization. The obtained data were analyzed using two-sample comparison of msFineAnalysis AI. Table 1 shows details of the measurement conditions.

Table 1 Measurement conditions

Pyrolyzer : EGA/PY-3030D (Frontier Lab)	
Sample amount	0.2mg
Furnace Temperature	600°C
Gas Chromatograph : 8890A GC (Agilent Technologies)	
Column	ZB-5MSi (Phenomenex)
	30m x 0.25mm, 0.25µm
Oven Temperature	40°C(2min)-10°C/min -320°C(30min)
Split ratio	100 : 1
Carrier gas	He, 1mL/min

Mass Spectrometer : JMS-T2000GC (JEOL)	
Ion Source	EI/FI combination ion source
Ionization	EI : 70eV
	FI : FI emitter, Flashing 12mA 30msec
IS Temperature	EI : 250°C, FI : No heating
GC-ITF Temperature	250°C
Mass Range	*m/z* 10-800
Drift compensation	EI : *m/z* 281.05, column bleed at end time
	FI : *m/z* 281.05, reservoir every 15min

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Results

Figure 1 shows the TIC chromatograms of the EI measurement results. The major pyrolysis products of PET, such as benzoic acid and vinyl benzoate, were detected in both samples. In addition to these, several other peaks were detected in the recycled PET product.

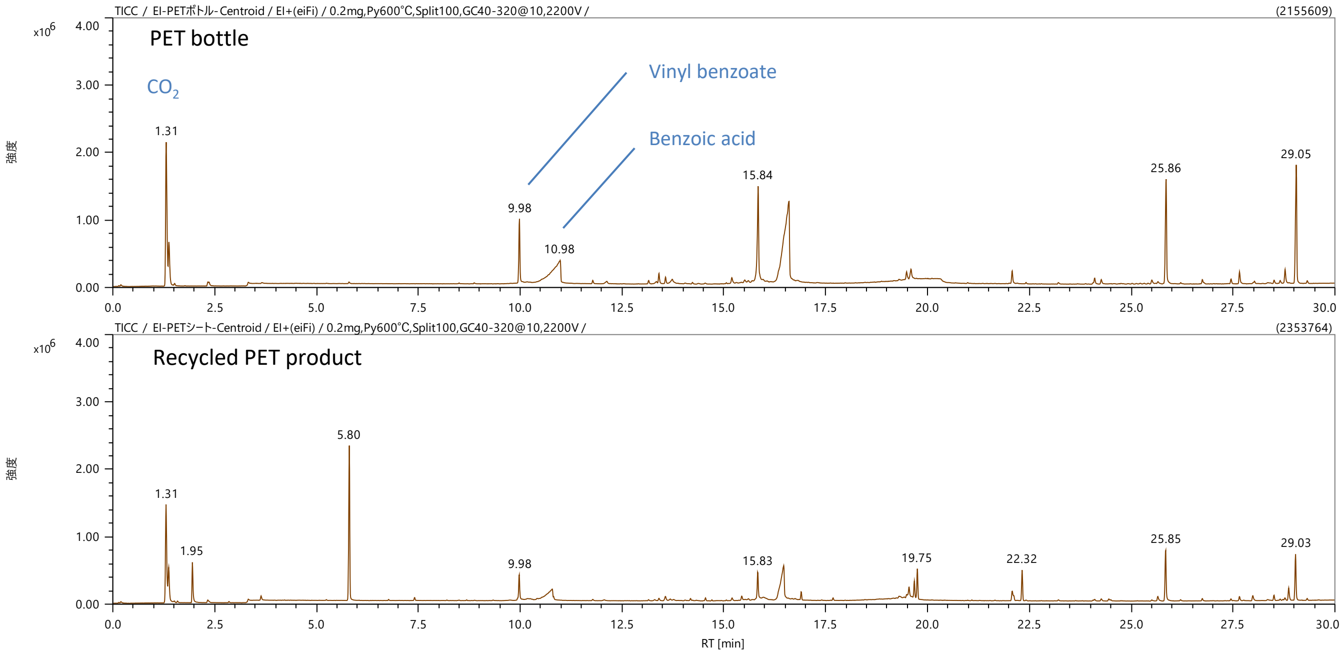

Figure 1 TIC chromatograms

Figure 2 shows the result window of two-sample comparison of msFineAnalysis AI.

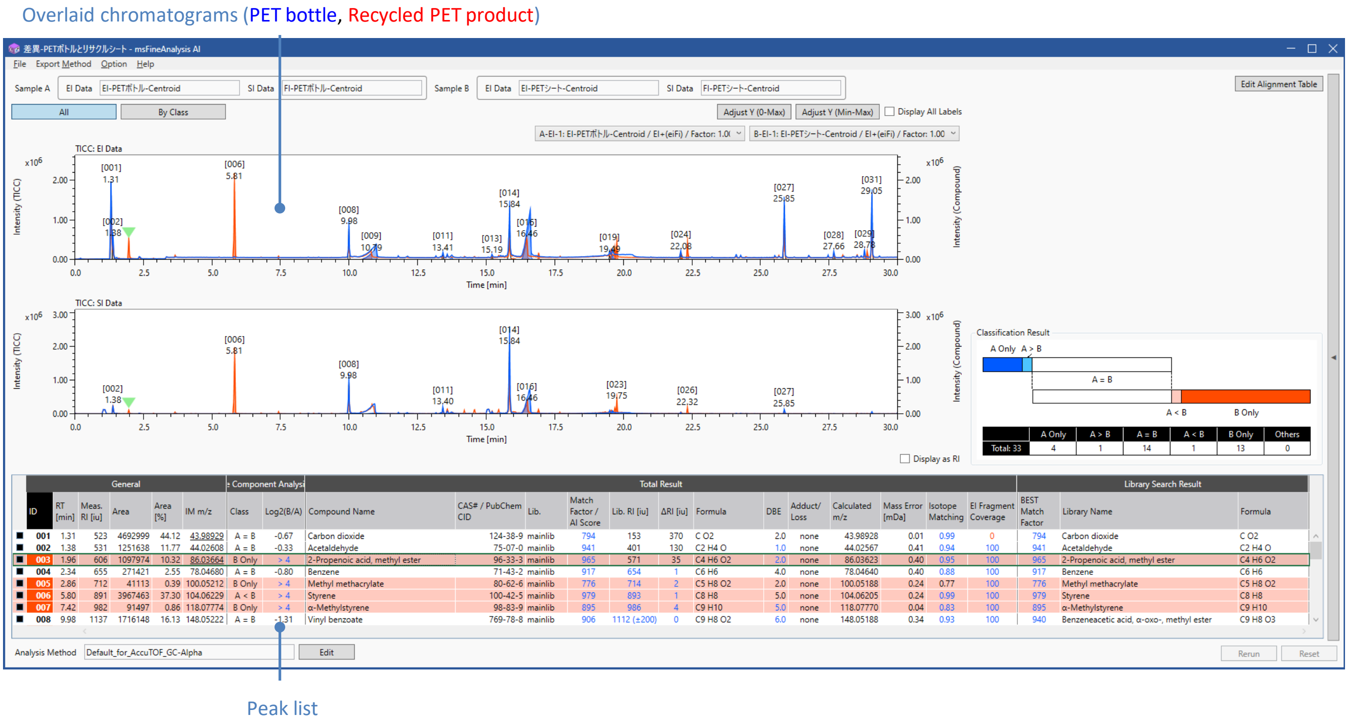

Figure 2 Result window of two-sample comparison

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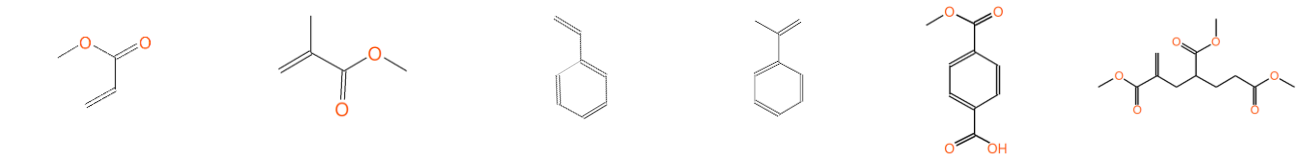
Table 2 shows the peak list, and Figure 3 shows the structural formulas of the compounds that were strongly detected in the recycled PET products (=Red group) . Methyl acrylate, styrene, and their hybrid trimers were identified, suggesting that recycled PET products may contain methyl acrylate-styrene (MS) copolymers.

Table 2 Peak list

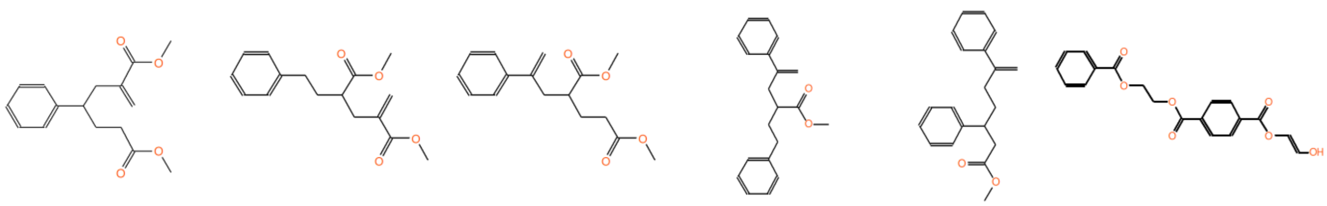
Blue : strong in PET bottle, Red : strong in recycled PET product, White : common components

General				e Component Analysi		Total Result											
ID	RT [min]	Meas. RI [iu]	Area [%]	Class	Log2(B/A)	Compound Name	CAS# / PubChem CID	Lib.	Match Factor / AI Score	Lib. RI [iu]	ΔRI [iu]	Formula	DBE	Calculated m/z	Mass Error [mDa]	Isotope Matching	EI Fragment Coverage
001	1.31	523	44.12	A = B	-0.67	Carbon dioxide	124-38-9	mainlib	794	153	370	C O2	2.0	43.98928	0.01	0.99	0
002	1.38	531	11.77	A = B	-0.33	Acetaldehyde	75-07-0	mainlib	941	401	130	C2 H4 O	1.0	44.02567	0.41	0.94	100
003	1.96	606	10.32	B Only	> 4	2-Propenoic acid, methyl ester	96-33-3	mainlib	965	571	35	C4 H6 O2	2.0	86.03623	0.40	0.95	100
004	2.34	655	2.55	A = B	-0.80	Benzene	71-43-2	mainlib	917	654	1	C6 H6	4.0	78.04640	0.40	0.88	100
005	2.86	712	0.39	B Only	> 4	Methyl methacrylate	80-62-6	mainlib	776	714	2	C5 H8 O2	2.0	100.05188	0.24	0.77	100
006	5.80	891	37.30	A < B	> 4	Styrene	100-42-5	mainlib	979	893	1	C8 H8	5.0	104.06205	0.24	0.99	100
007	7.42	982	0.86	B Only	> 4	α-Methylstyrene	98-83-9	mainlib	895	986	4	C9 H10	5.0	118.07770	0.04	0.83	100
008	9.98	1137	16.13	A = B	-1.31	Vinyl benzoate	769-78-8	mainlib	906	1112 (±200)	0	C9 H8 O2	6.0	148.05188	0.34	0.93	100
010	10.97	1201	41.68	A = B	-1.50	Benzoic acid	65-85-0	mainlib	953	1172	29	C7 H6 O2	5.0	122.03623	0.26	N/A	100
011	13.41	1373	3.14	A = B	-1.87	Vinyl trans-cinnamate	17719-70-9	mainlib	906	1318 (±200)	0	C11 H10 O2	7.0	174.06753	0.39	0.87	100
012	13.73	1397	3.19	A Only	< -4	4-Vinylbenzoic acid	1075-49-6	mainlib	911	1291 (±219)	0	C9 H8 O2	6.0	148.05188	0.29	0.93	100
013	15.19	1512	2.35	A = B	-1.17	ethenyl 4-acetylbenzoate	19093261	AI	872	1536 (±95)	0	C11 H10 O3	7.0	190.06245	0.74	0.85	100
014	15.84	1565	30.80	A = B	-1.98	bis(ethenyl) benzene-1,4-dicarboxylate	15374889	AI	889	1625 (±95)	0	C12 H10 O4	8.0	218.05736	0.37	0.98	100
015	15.98	1576	3.73	B Only	> 4	1,4-Benzenedicarboxylic acid, methyl ester	1679-64-7	mainlib	798	1569	7	C9 H8 O4	6.0	180.04171	-0.42	N/A	100
	16.59	1628	100.00	A = B	-1.77	4-ethenoxycarbonylbenzoic acid	22223159	AI	924	1650 (±95)	0	C10 H8 O4	7.0	192.04171	0.30	0.90	100
018	16.90	1655	2.55	B Only	> 4	trimethyl hex-5-ene-1,3,5-tricarboxylate	11425398	AI	679	1681 (±95)	0	C12 H18 O6	4.0	258.10979	0.60	0.76	100
019	19.49	1893	2.04	A = B	-1.29	ethenyl 4-phenylbenzoate	19093270	AI	911	1932 (±95)	0	C15 H12 O2	10.0	224.08318	0.19	0.89	83
020	19.55	1899	4.40	B Only	> 4	dimethyl 2-methylene-4-phenylheptanedioate	-	User	994	1899	0	C16 H20 O4	7.0	276.13561	0.57	0.80	95
021	19.59	1903	5.00	A Only	< -4	Biphenyl-4-carboxylic acid	92-92-2	mainlib	870	1737 (±219)	0	C13 H10 O2	9.0	198.06753	0.40	0.71	100
022	19.68	1912	3.73	B Only	> 4	dimethyl 2-methylene-4-phenethylpentanedioate	-	User	981	1912	0	C16 H20 O4	7.0	276.13561	0.50	0.48	100
023	19.75	1919	7.84	B Only	> 4	dimethyl 2-(2-phenylallyl)pentanedioate	-	User	999	1919	0	C16 H20 O4	7.0	276.13561	0.51	0.96	100
024	22.08	2163	3.98	A = B	-0.37	1,2-Ethanediol, dibenzoate	94-49-5	mainlib	906	2108	55	C16 H14 O4	10.0	270.08866	0.24	0.79	100
025	22.12	2168	1.58	B Only	> 4	:methyl 4,6-diphenylhept-6-enoate	-	User	986	2168	0	C20 H22 O2	10.0	-	-	-	100
026	22.32	2190	7.87	B Only	> 4	methyl 2-phenethyl-4-phenylpent-4-enoate	-	User	999	2189	1	C20 H22 O2	10.0	294.16143	0.51	0.88	100
027	25.85	2618	31.33	A = B	-1.15	1-O-(2-benzoyloxyethyl) 4-O-ethenyl benzene-1,4-dicarboxylate	101115782	AI	554	2691 (±95)	0	C19 H16 O6	12.0	340.09414	0.08	0.77	100
028	27.66	2866	3.96	A = B	-1.49	ethyl 3-(acetyloxymethyl)-4-oxo-2-phenylchromene-8-carboxylate	19972752	AI	399	2917 (±95)	0	C21 H18 O6	13.0	366.10979	-0.55	N/A	100
029	28.78	3029	5.13	A > B	-2.44	[PY] PET	-	AI	266	3006 (±95)	0	C20 H16 O7	13.0	368.08905	-	-	100
030	28.88	3044	4.02	B Only	> 4	[PY] PET	-	AI	381	3052 (±95)	0	C19 H16 O7	12.0	356.08905	-	-	100
031	29.05	3071	36.45	A = B	-1.53	ethan-1,2-diyl divinyl diterephthalate	-	User	999	3071	0	C22 H18 O8	14.0	410.09962	0.61	0.76	100
032	31.77	3464	2.44	A = B	-1.59	(5,7-dimethoxy-1-oxo-3,4-diphenylisochromen-6-yl) acetate	102581926	AI	457	3356 (±95)	13	C25 H20 O6	16.0	416.12544	-1.62	N/A	100
033	34.63	3742	4.99	A = B	-0.21	bis(2-benzoyloxyethyl) benzene-1,4-dicarboxylate	-	User	994	3742	0	C26 H22 O8	16.0	462.13092	1.89	N/A	100

mainlib = The compound name and structural formula obtained by NIST library, AI = AI predicted library, User = Manually edited library



003 Methyl acrylate : M | 005 Methyl methacrylate | 006 Styrene : S | 007 Methyl styrene | 015 | 018 M trimer



020 MSM trimer | 022 MMS trimer | 023 SMM trimer | 025 SMS trimer | 026 SSM trimer | 030

Figure 3 Structural formulas (Red : strong in recycled PET product)

Conclusion

PET bottles and recycled PET product were analyzed using two-sample comparison of msFineAnalysis AI. As a result, it was confirmed that recycled PET products may contain MS copolymer. This recycled PET product is a thin and high-performance buffer sheet, which corresponds to upcycling. It was thought that MS copolymer was blended to improve moldability and weather resistance.