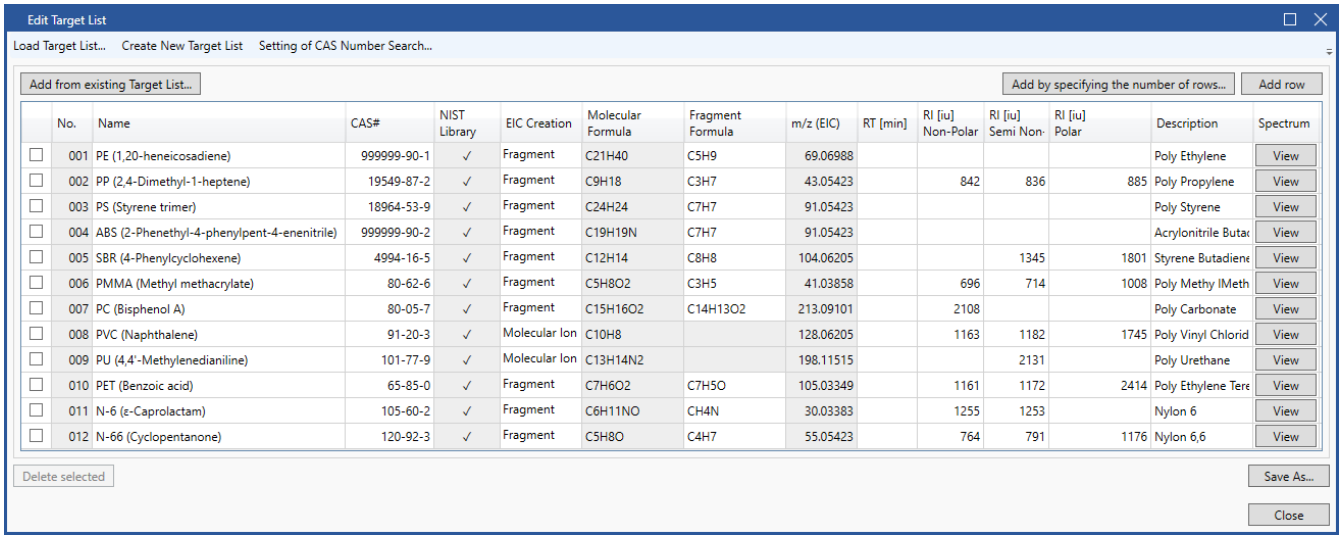
Target analysis of msFineAnalysis AI Ver.2
② Polymer type estimation

Product used: Mass Spectrometer (MS)

Introduction

The target analysis function of the unknown compounds structure analysis software "msFineAnalysis AI" Ver.2 detects peaks from extracted ion chromatograms (EICs) based on information such as the molecular formulas and mass spectra of pre-listed components. In the previous MSTips478, we introduced an application using the software preset target list "Polymer additives".

These target lists can be edited by the user, and new ones can be created for different purposes. In this MSTips we will introduce an application of polymer type estimation using the major pyrolysis products of polymers [1)]. Figure 1 shows a target list for this application. No. 001 1,20-heneicosadiene of polyethylene (PE) and No. 004 2-Phenethyl-4-phenylpent-4-enenitrile of acrylonitrile butadiene styrene (ABS) are not registered in the NIST library, but by registering the measurement results in advance in the NIST user library, it become possible to judge using mass spectrum similarity. Furthermore, by specifying a high-intensity fragment ion instead of a molecular ion as the extracted ion, it possible more sensitive peak detection.



	No.	Name	CAS#	NIST Library	EIC Creation	Molecular Formula	Fragment Formula	m/z (EIC)	RT [min]	RI [iu] Non-Polar	RI [iu] Semi Non-	RI [iu] Polar	Description	Spectrum
☐	001	PE (1,20-heneicosadiene)	999999-90-1	✓	Fragment	C21H40	C5H9	69.06988					Poly Ethylene	View
☐	002	PP (2,4-Dimethyl-1-heptene)	19549-87-2	✓	Fragment	C9H18	C3H7	43.05423		842	836	885	Poly Propylene	View
☐	003	PS (Styrene trimer)	18964-53-9	✓	Fragment	C24H24	C7H7	91.05423					Poly Styrene	View
☐	004	ABS (2-Phenethyl-4-phenylpent-4-enenitrile)	999999-90-2	✓	Fragment	C19H19N	C7H7	91.05423					Acrylonitrile Buta	View
☐	005	SBR (4-Phenylcyclohexene)	4994-16-5	✓	Fragment	C12H14	C8H8	104.06205			1345	1801	Styrene Butadiene	View
☐	006	PMMA (Methyl methacrylate)	80-62-6	✓	Fragment	C5H8O2	C3H5	41.03858		696	714	1008	Poly Methy IMeth	View
☐	007	PC (Bisphenol A)	80-05-7	✓	Fragment	C15H16O2	C14H13O2	213.09101		2108			Poly Carbonate	View
☐	008	PVC (Naphthalene)	91-20-3	✓	Molecular Ion	C10H8		128.06205		1163	1182	1745	Poly Vinyl Chlorid	View
☐	009	PU (4,4'-Methylenedianiline)	101-77-9	✓	Molecular Ion	C13H14N2		198.11515			2131		Poly Urethane	View
☐	010	PET (Benzoic acid)	65-85-0	✓	Fragment	C7H6O2	C7H5O	105.03349		1161	1172	2414	Poly Ethylene Tere	View
☐	011	N-6 (ε-Caprolactam)	105-60-2	✓	Fragment	C6H11NO	CH4N	30.03383		1255	1253		Nylon 6	View
☐	012	N-66 (Cyclopentanone)	120-92-3	✓	Fragment	C5H8O	C4H7	55.05423		764	791	1176	Nylon 6,6	View

Figure 1 Target list for polymer type estimation

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Experiment

As the sample, commercially available polypropylene (PP), recycled PP, polyethylene terephthalate (PET), and recycled PET products 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 was analyzed using 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	600ºC
Gas Chromatograph : 8890A GC (Agilent Technologies)	
Column	ZB-5MSi (Phenomenex)
	30m x 0.25mm, 0.25µm
Oven Temperature	40ºC(2min)-10ºC/min -320ºC(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 : 250ºC, FI : No heating
GC-ITF Temperature	250ºC
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

Results

Figure 2 shows the TIC chromatograms of the EI measurement results. 2,4-Dimethyl-1-heptene, a major pyrolysis product of PP, was detected in PP and recycled PP products. CO2, vinyl benzoate, and benzoic acid, major pyrolysis products of PET, were detected in PET and recycled PET products. In addition to these, several other peaks were detected in recycled PET product.

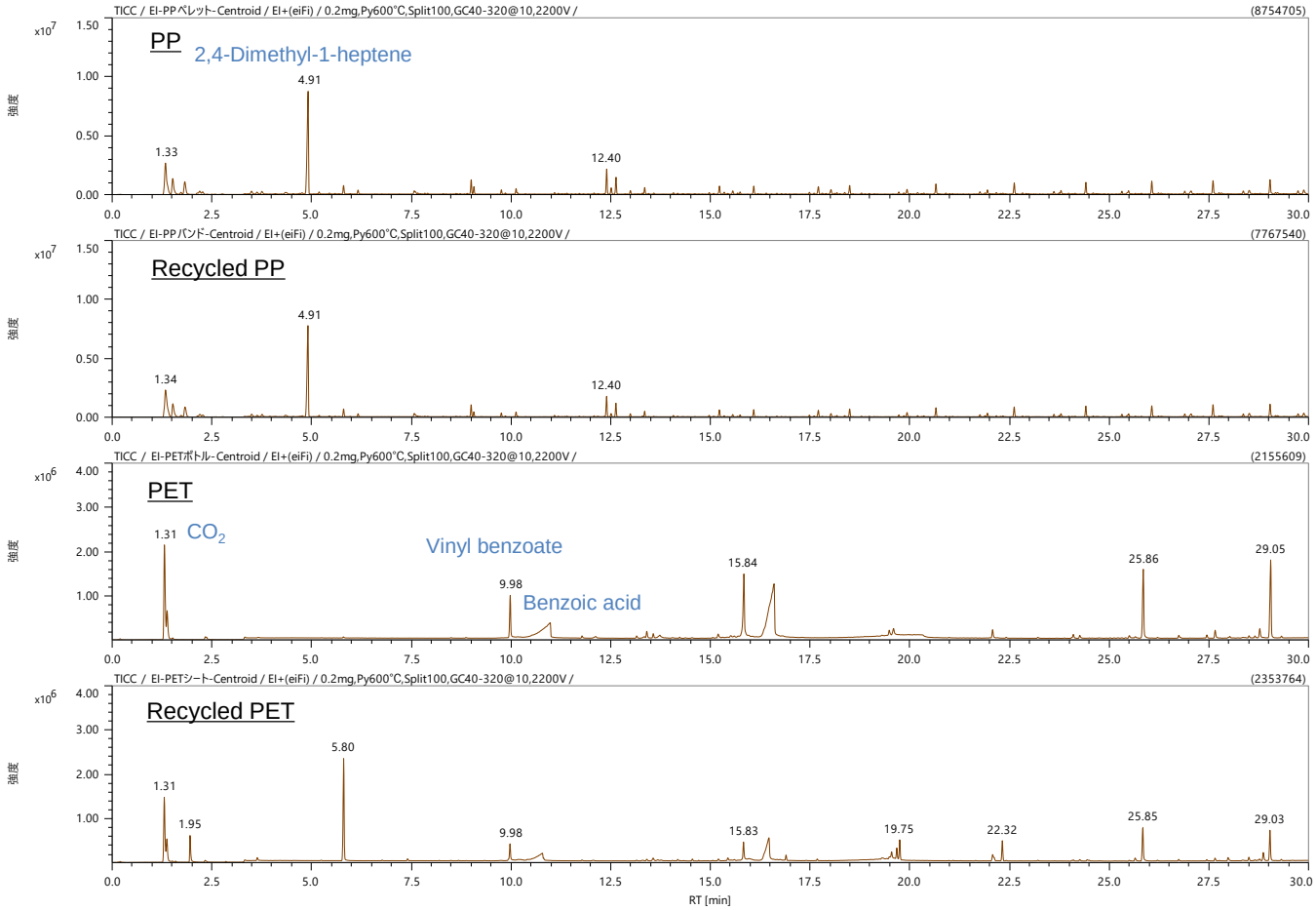

Figure 2 TIC chromatograms

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Target analysis results ① – PP product

Figure 3 shows the results window of the target analysis of msFineAnalysis AI.

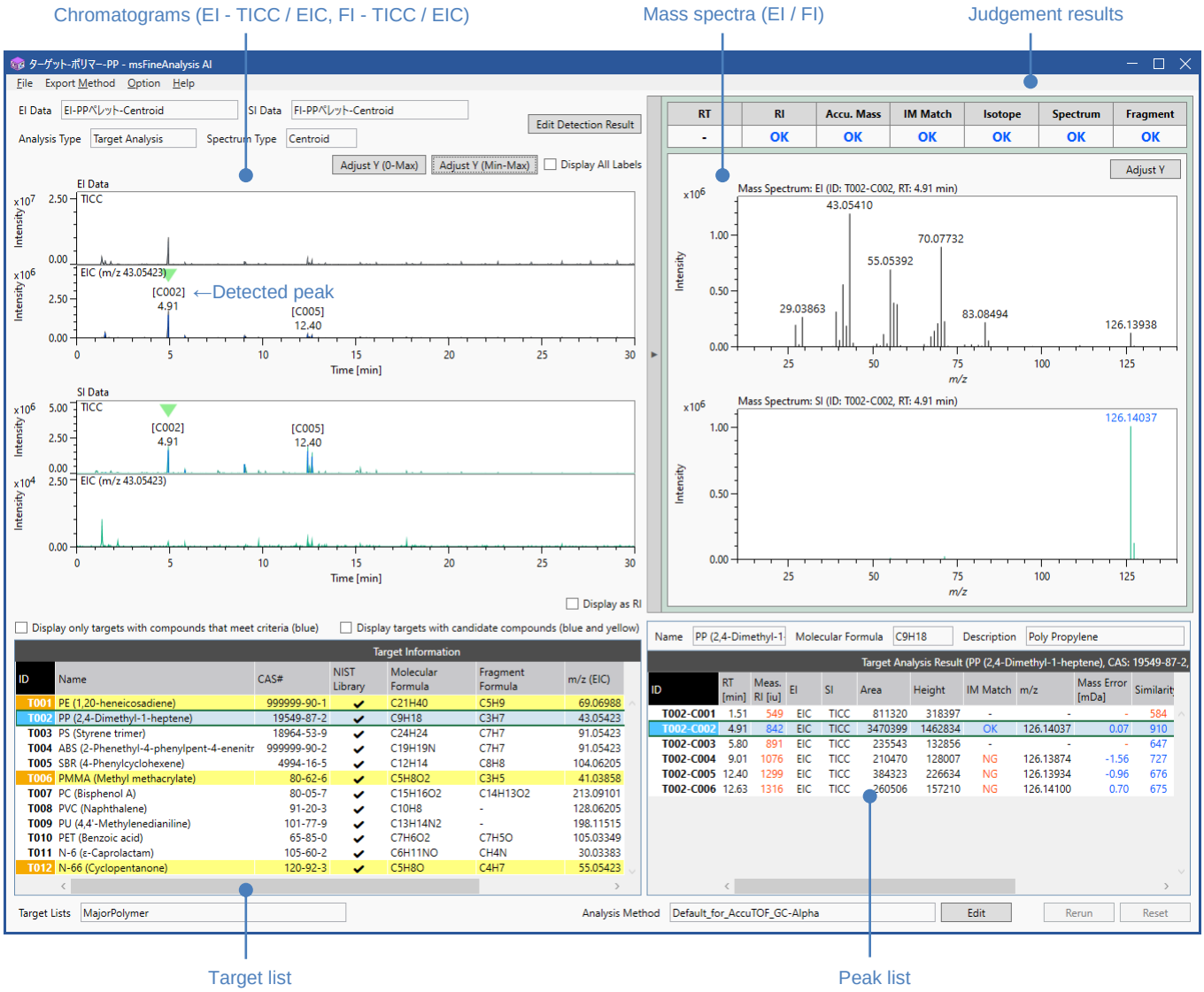

Figure 3 Result window of target analysis

Table 2 shows the target list of the analysis results. The background color reflects the analysis results. Yellow indicates compounds with peaks detected on the EIC, and blue indicates compounds that also passed qualitative analysis such as mass spectrum similarity (=compound identified to be targets). In this result, only 2,4-dimethyl-1-heptene, a major pyrolysis product of PP, was identified.

Table 2 Target list

Target Information									
ID	Name	CAS#	NIST Library	Molecular Formula	Fragment Formula	m/z (EIC)	Description	Num. of Detected	Num. of Passed
T001	PE (1,20-heneicosadiene)	999999-90-1	✓	C21H40	C5H9	69.06988	Poly Ethylene	14	0
T002	PP (2,4-Dimethyl-1-heptene)	19549-87-2	✓	C9H18	C3H7	43.05423	Poly Propylene	6	1
T003	PS (Styrene trimer)	18964-53-9	✓	C24H24	C7H7	91.05423	Poly Styrene	0	0
T004	ABS (2-Phenethyl-4-phenylpent-4-enenitrile)	999999-90-2	✓	C19H19N	C7H7	91.05423	Acrylonitrile Butadiene Styrene copolymer	0	0
T005	SBR (4-Phenylcyclohexene)	4994-16-5	✓	C12H14	C8H8	104.06205	Styrene Butadiene Rubber	0	0
T006	PMMA (Methyl methacrylate)	80-62-6	✓	C5H8O2	C3H5	41.03858	Poly Methy lMethAcrylate	5	0
T007	PC (Bisphenol A)	80-05-7	✓	C15H16O2	C14H13O2	213.09101	Poly Carbonate	0	0
T008	PVC (Naphthalene)	91-20-3	✓	C10H8	-	128.06205	Poly Vinyl Chloride	0	0
T009	PU (4,4'-Methylenedianiline)	101-77-9	✓	C13H14N2	-	198.11515	Poly Urethane	0	0
T010	PET (Benzoic acid)	65-85-0	✓	C7H6O2	C7H5O	105.03349	Poly Ethylene Terephthalate	0	0
T011	N-6 (ε-Caprolactam)	105-60-2	✓	C6H11NO	CH4N	30.03383	Nylon 6	0	0
T012	N-66 (Cyclopentanone)	120-92-3	✓	C5H8O	C4H7	55.05423	Nylon 6,6	3	0

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Target analysis results ② – recycled PP product

Table 3 shows the target list of the analysis results. As with PP product, only 2,4-dimethyl-1-heptene was identified.

Table 3 Target list

Target Information									
ID	Name	CAS#	NIST Library	Molecular Formula	Fragment Formula	m/z (EIC)	Description	Num. of Detected	Num. of Passed
T001	PE (1,20-heneicosadiene)	999999-90-1	✓	C21H40	C5H9	69.06988	Poly Ethylene	13	0
T002	PP (2,4-Dimethyl-1-heptene)	19549-87-2	✓	C9H18	C3H7	43.05423	Poly Propylene	6	1
T003	PS (Styrene trimer)	18964-53-9	✓	C24H24	C7H7	91.05423	Poly Styrene	0	0
T004	ABS (2-Phenethyl-4-phenylpent-4-enenitrile)	999999-90-2	✓	C19H19N	C7H7	91.05423	Acrylonitrile Butadiene Styrene copolymer	0	0
T005	SBR (4-Phenylcyclohexene)	4994-16-5	✓	C12H14	C8H8	104.06205	Styrene Butadiene Rubber	0	0
T006	PMMA (Methyl methacrylate)	80-62-6	✓	C5H8O2	C3H5	41.03858	Poly Methy lMethAcrylate	5	0
T007	PC (Bisphenol A)	80-05-7	✓	C15H16O2	C14H13O2	213.09101	Poly Carbonate	0	0
T008	PVC (Naphthalene)	91-20-3	✓	C10H8	-	128.06205	Poly Vinyl Chloride	0	0
T009	PU (4,4'-Methylenedianiline)	101-77-9	✓	C13H14N2	-	198.11515	Poly Urethane	0	0
T010	PET (Benzoic acid)	65-85-0	✓	C7H6O2	C7H5O	105.03349	Poly Ethylene Terephthalate	0	0
T011	N-6 (ε-Caprolactam)	105-60-2	✓	C6H11NO	CH4N	30.03383	Nylon 6	0	0
T012	N-66 (Cyclopentanone)	120-92-3	✓	C5H8O	C4H7	55.05423	Nylon 6,6	2	0

Target analysis results ③ – PET product

Table 4 shows the target list of the analysis results. Only benzylic acid, a major pyrolysis product of PET, was identified.

Table 4 Target list

Target Information									
ID	Name	CAS#	NIST Library	Molecular Formula	Fragment Formula	m/z (EIC)	Description	Num. of Detected	Num. of Passed
T001	PE (1,20-heneicosadiene)	999999-90-1	✓	C21H40	-	292.31245	Poly Ethylene	0	0
T002	PP (2,4-Dimethyl-1-heptene)	19549-87-2	✓	C9H18	-	126.14030	Poly Propylene	0	0
T003	PS (Styrene trimer)	18964-53-9	✓	C24H24	-	312.18725	Poly Styrene	0	0
T004	ABS (2-Phenethyl-4-phenylpent-4-enenitrile)	999999-90-2	✓	C19H19N	-	261.15120	Acrylonitrile Butadiene Styrene copolymer	0	0
T005	SBR (4-Phenylcyclohexene)	4994-16-5	✓	C12H14	-	158.10900	Styrene Butadiene Rubber	0	0
T006	PMMA (Methyl methacrylate)	80-62-6	✓	C5H8O2	-	100.05188	Poly Methy lMethAcrylate	0	0
T007	PC (Bisphenol A)	80-05-7	✓	C15H16O2	-	228.11448	Poly Carbonate	1	0
T008	PVC (Naphthalene)	91-20-3	✓	C10H8	-	128.06205	Poly Vinyl Chloride	2	0
T009	PU (4,4'-Methylenedianiline)	101-77-9	✓	C13H14N2	-	198.11515	Poly Urethane	0	0
T010	PET (Benzoic acid)	65-85-0	✓	C7H6O2	-	122.03623	Poly Ethylene Terephthalate	30	1
T011	N-6 (ε-Caprolactam)	105-60-2	✓	C6H11NO	-	113.08352	Nylon 6	0	0
T012	N-66 (Cyclopentanone)	120-92-3	✓	C5H8O	-	84.05697	Nylon 6,6	0	0

Target analysis results ④ – recycled PET product

Table 5 shows the target list of the analysis results. As with PET product, benzoic acid was identified. In addition, styrene trimer of polystyrene (PS) and methyl methacrylate of polymethyl methacrylate (PMMA) were identified, suggesting that PS and PMMA may be included.

Table 5 Target list

Target Information								
ID	Name	CAS#	NIST Library	Molecular Formula	m/z (EIC)	Description	Num. of Detected	Num. of Passed
T001	PE (1,20-heneicosadiene)	999999-90-1	✓	C21H40	292.31245	Poly Ethylene	0	0
T002	PP (2,4-Dimethyl-1-heptene)	19549-87-2	✓	C9H18	126.14030	Poly Propylene	0	0
T003	PS (Styrene trimer)	18964-53-9	✓	C24H24	312.18725	Poly Styrene	1	1
T004	ABS (2-Phenethyl-4-phenylpent-4-enenitrile)	999999-90-2	✓	C19H19N	261.15120	Acrylonitrile Butadiene Styrene copolymer	0	0
T005	SBR (4-Phenylcyclohexene)	4994-16-5	✓	C12H14	158.10900	Styrene Butadiene Rubber	1	0
T006	PMMA (Methyl methacrylate)	80-62-6	✓	C5H8O2	100.05188	Poly Methy lMethAcrylate	2	1
T007	PC (Bisphenol A)	80-05-7	✓	C15H16O2	228.11448	Poly Carbonate	0	0
T008	PVC (Naphthalene)	91-20-3	✓	C10H8	128.06205	Poly Vinyl Chloride	5	0
T009	PU (4,4'-Methylenedianiline)	101-77-9	✓	C13H14N2	198.11515	Poly Urethane	0	0
T010	PET (Benzoic acid)	65-85-0	✓	C7H6O2	122.03623	Poly Ethylene Terephthalate	27	1
T011	N-6 (ε-Caprolactam)	105-60-2	✓	C6H11NO	113.08352	Nylon 6	1	0
T012	N-66 (Cyclopentanone)	120-92-3	✓	C5H8O	84.05697	Nylon 6,6	0	0

Conclusion

Polymer type estimation was performed using target analysis of msFineAnalysis AI Ver.2. As a result, it was confirmed that recycled PET products may contain polymers such as PPS and PMMA. Non-targeted analysis is necessary to obtain more detailed information, but targeted analysis can quickly obtain results and is effective as a screening method.

Reference

1) Shin Tsuge, Hajime Ohtani, Chuichi Watanabe (2011), Pyrolysis - GC/MS Data Book of Synthetic Polymers, Elsevier

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