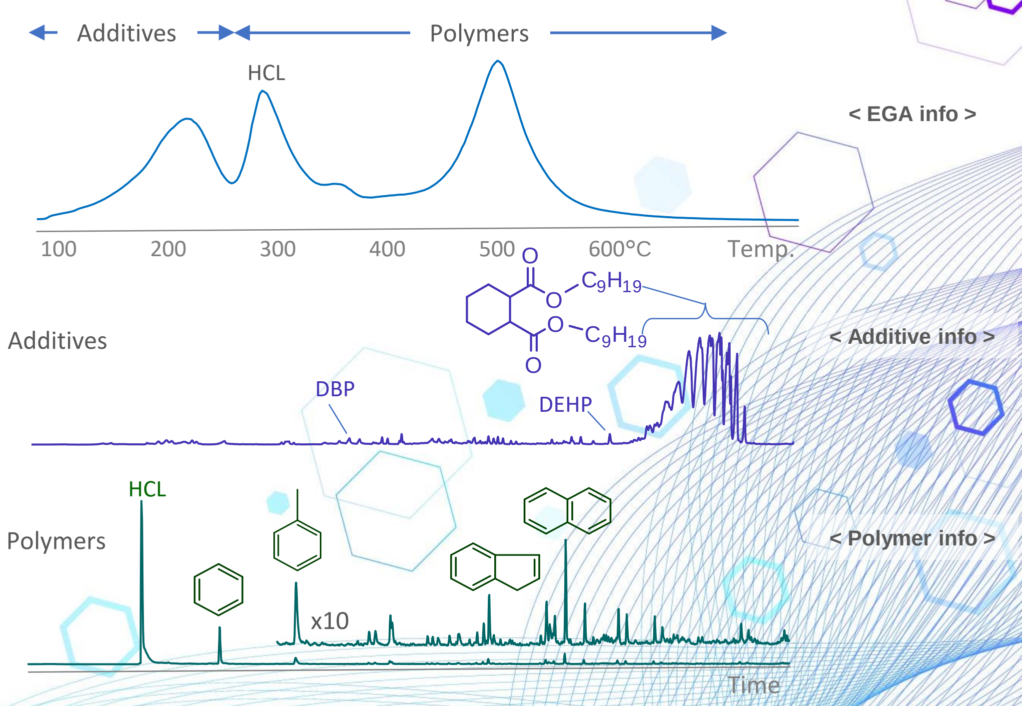
FRONTIER LAB

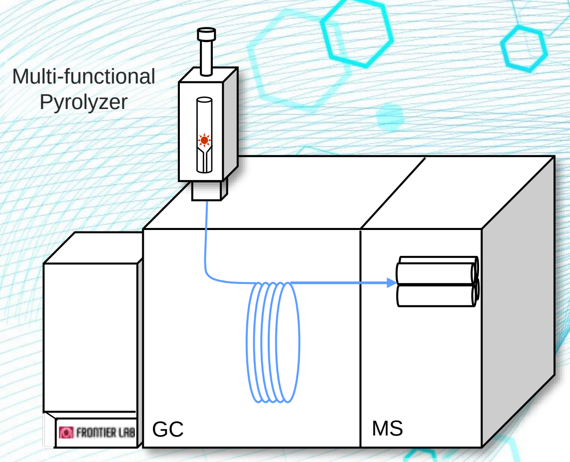
1315 polymers and 590 additives are stored in libraries

F-Search System

Search software F-Search (Ver. 3.7) that supports polymer analysis, and varied types of libraries:

Evolved gas (polymers), thermal desorption (additives), and pyrolysis (polymers)





Multi-functional Pyrolysis System

F-Search System

"F-Search System" (Search program for polymers and additives)

The qualitative analysis of unknown polymeric materials is performed using a variety of methods such as IR, NMR, thermal analysis, and pyrolysis (Py)-GC. Polymeric material containing cross-linked or network polymers, or with complex additive packages, are best characterized using the Multi-functional pyrolyzer that allows you to use techniques such as Py-GC, thermal desorption (TD)-GC and evolved gas analysis (EGA).

However, interpretation of the pyrogram or EGA thermogram is a difficult task, requiring professional intuition and experience. Frontier Laboratories has now upgraded F-Search (Ver. 3.7). 315 new polymers have been added to the polymer libraries, 100 vulcanization accelerators for rubber and azo dyes have been added to Additive library, and 165 polymers measured on UA-WAX columns have been added to Pyrolyzate library.

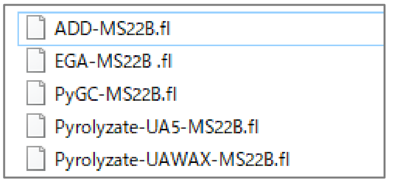
Eight Unique Advantages of F-Search System (Patents: 3801355 Japan, 6444979 US)

1. F-Search system consists of search software and four unique libraries and allows users to select among them for specific purposes.

- **Search software: F-Search**
- **Libraries**

Polymer analysis
- Pyrogram library
- EGA library
- Pyrolyzates library
  - UA-5 Column
  - UA-WAX Column

Additives analysis --- Additive library



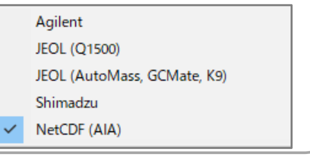
The reliability of analysis results is greatly improved by evaluating data obtained by different analytical techniques. Search results such as mass spectra, pyrograms and thermograms of candidate compounds can be displayed side-by-side for easy visual comparison. Further, the system allows users to effortlessly construct their own libraries.

2. The search software F-Search allows you to quickly search different types of data such as pyrograms and EGA data. It can also accommodate various GC/MS data formats for your convenience.

Because the unique search algorithm is used to compare mass spectra, candidate compounds are instantly displayed. Also, the search can be simultaneously performed across multiple libraries.

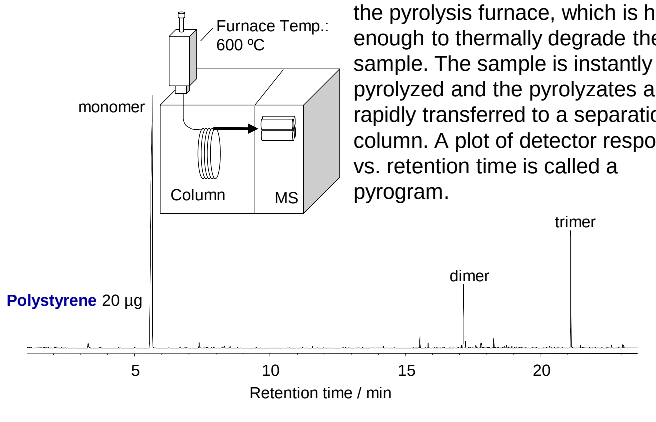
GC/MS data formats of Agilent, Shimadzu, and JEOL can be directly read without any translation or conversion, while other data formats can also be read upon converting to AIA format (NetCDF) files using software from their own companies.

Compatible with major GC/MS systems



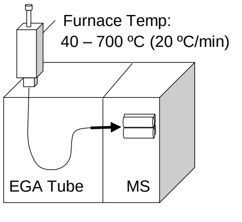
1 : What is Py-GC?

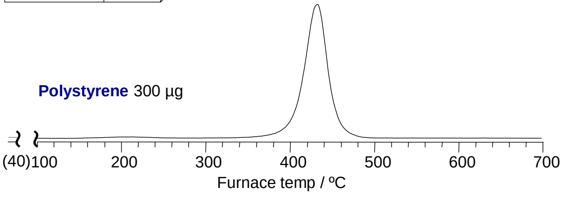
Py-GC is a method used to obtain a pyrogram. In this method, the sample is placed in a sample cup. It is kept at the ambient temperature until it is introduced into the center of the pyrolysis furnace, which is hot enough to thermally degrade the sample. The sample is instantly pyrolyzed and the pyrolyzates are rapidly transferred to a separation column. A plot of detector response vs. retention time is called a pyrogram.



2 : What is EGA?

EGA is a simple thermal analysis method where the temperature of the sample is continuously raised, and the evolved gases are directly measured. A plot of detector response vs. sample temperature is called a thermogram. As shown in the figure, the pyrolyzer and the MS are connected by a short 2.5 m deactivated EGA tube (0.15 mm i.d.) in the oven where the temperature is maintained at 300 ºC.





3. Search results obtained by the unique search algorithm employed in F-Search are unaffected by changes in analytical conditions.

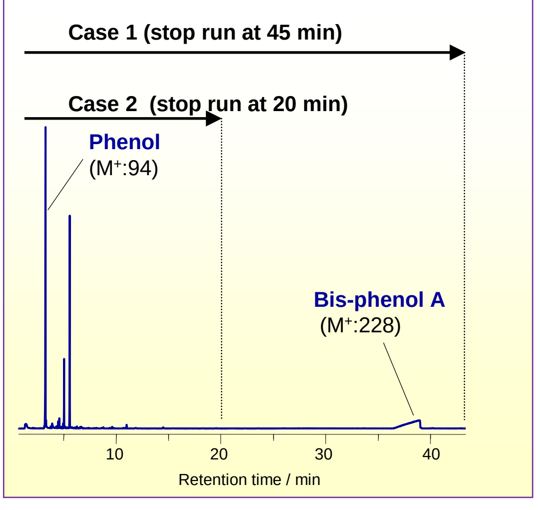
Generally, retention times are greatly influenced by changes in analytical conditions and separation columns; however, due to the unique patented search algorithm, the search results are not affected by the use of different separation columns or analytical conditions. Data 1 and Data 2 are mass spectra from the same unknown polymer. The mass spectra derived by this algorithm are very similar even though they were obtained using different GC analytical conditions. In both cases, the unknown polymer is identified as “BT resin.” Data 1 compares the search results from Case 1 and Case 2. In both Cases 1 and 2, BT resin was the first candidate. The library contains three sets of mass spectra for the retention times of C1 - C10, C1 - C20, and C1 - C40, so even if a compound with a high boiling point is missing, as in Case 2, equivalent results can be obtained. As these results show, F-Search can be used to reliably identify polymers using data obtained under different analytical conditions.

Data 1 and Data 2 are pyrograms of the same unknown polymer obtained using different GC conditions.

Data 1

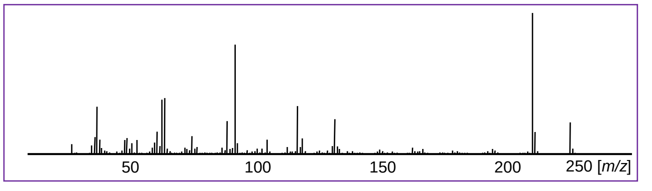
Furnace temp.: 600 ºC, Col: UA-5 (MS/HT) (*L*=30 m, i.d.=0.25 mm, df=0.25 µm)

GC Oven: 60 - 170ºC (20ºC/min)



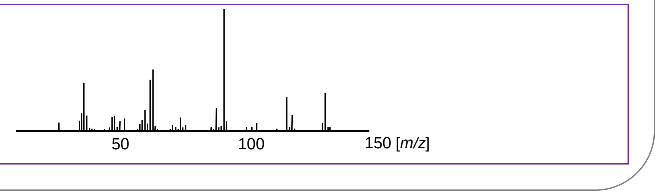
Case 1 (mass spectrum of the peaks detected from 0 to 45 min)

	Polymer/Additive	Qual[%]	EntryID
1	Bismaleimide-triazine resin ; BT (C1-C40)	91.3	FLK-338
2	Bismaleimide triazine resin ; BT resin (C1-C40)	87.7	FLT-107
3	Polycarbonate ; PC [Carbon fibre reinforced] (C1-C40)	69.3	FLK-144
4	Polycarbonate ; PC (C1-C40)	68.8	FLG-702
5	Polycarbonate(melt method) ; MM-PC (C1-C40)	67.1	FLT-127



Case 2 (mass spectrum of the peaks detected from 0 to 20 min)

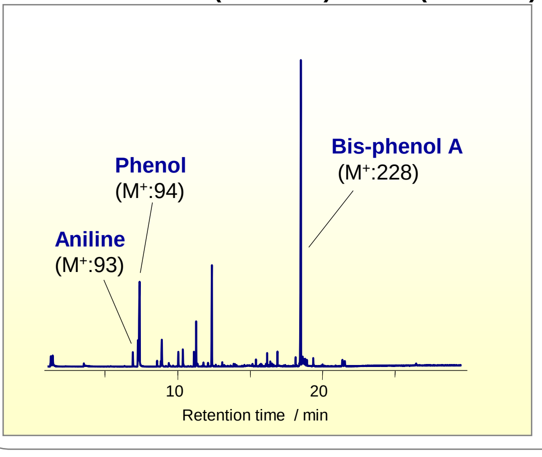
	Polymer/Additive	Qual[%]	EntryID
1	Bismaleimide-triazine resin ; BT (C1-C20)	90.2	FLK-338
2	Bismaleimide triazine resin ; BT resin (C1-C20)	83.8	FLT-107
3	Polyetheretherketone ; PEEK (C1-C40)	82.9	FLK-273
4	Polyetheretherketone ; PEEK (C1-C20)	81.9	FLK-273
5	Polyethersulfone ; PESF (C1-C10)	81.9	FLG-705



Data 2

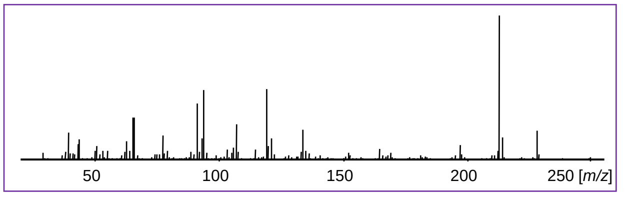
Furnace temp.: 600 ºC, Col: UA-5 (MS/HT) (*L*=30 m, i.d.=0.25 mm, df=0.25 µm)

GC Oven: 40 - 140 (10ºC/min) - 320ºC(20ºC/min)



Mass spectrum created from all the peaks detected

	Polymer/Additive	Qual[%]	EntryID
1	Bismaleimide triazine resin ; BT resin (C1-C40)	95.6	FLT-107
2	Bismaleimide-triazine resin ; BT (C1-C40)	95.1	FLK-338
3	Polycarbonate ; PC (C1-C40)	83.9	FLG-702
4	Polycarbonate (solvent method) ; SM-PC (C1-C40)	81.8	FLT-128
5	Polycarbonate ; PC [Carbon fibre reinforced] (C1-C40)	81.6	FLK-144

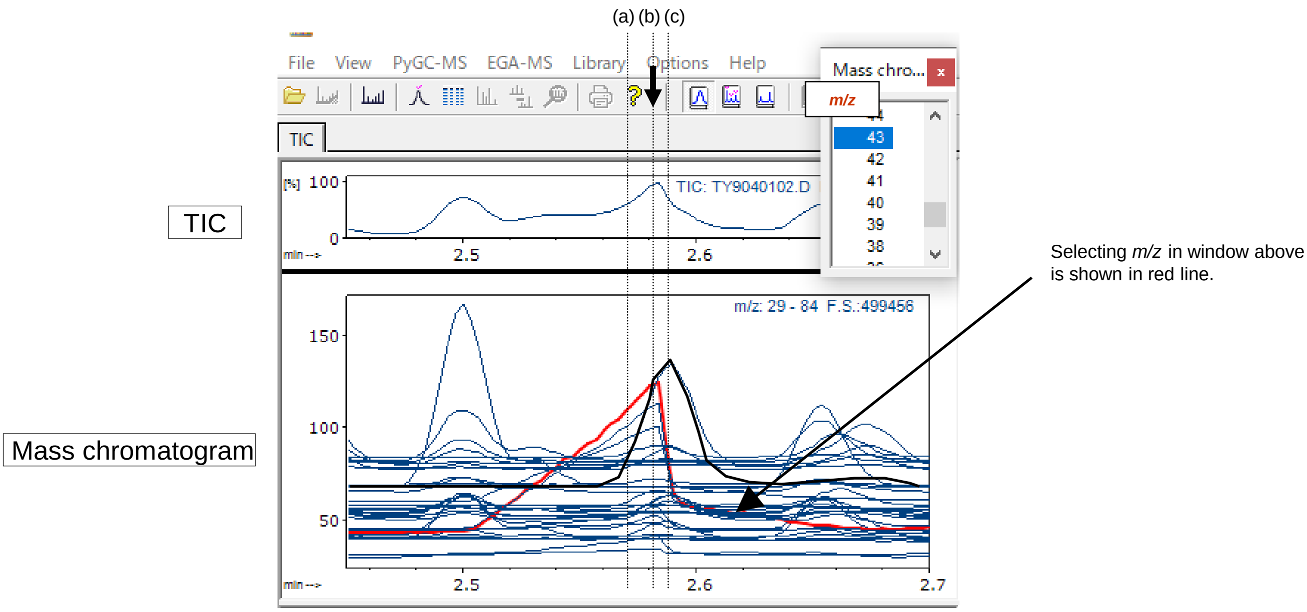


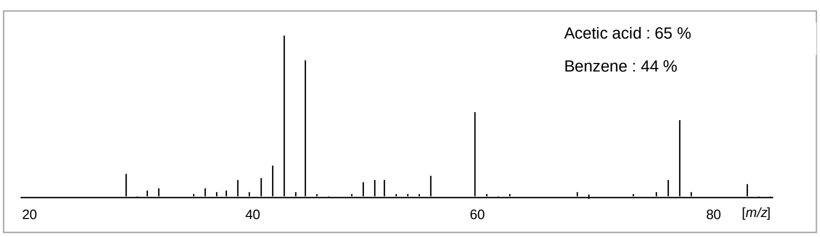
4. Two-dimensional multi-ion chromatograms allow you to obtain high quality mass spectra from overlapping peaks.

Pyrograms generally consist of complex pyrolyzates; therefore, it is very important to obtain high quality mass spectra of the targeted peak. F-Search displays TIC and mass chromatogram on a single screen, and also allows you to subtract surrounding peaks from the targeted peak to obtain a high-quality mass spectrum. An example is shown below to illustrate this feature.

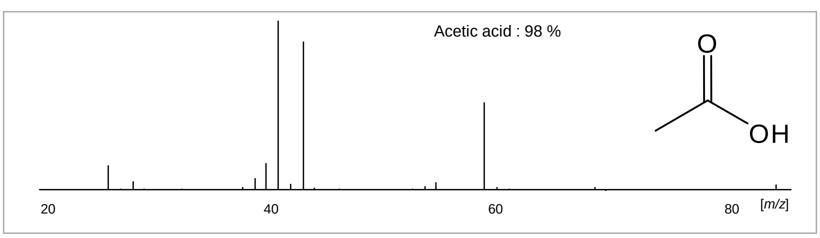
To identify the compound of the peak marked with an arrow shown in the TIC, a search was made on the average spectrum between (a) and (c). The search result obtained was acetic acid with 65% match quality and benzene with 44% match quality. Then, a two-dimensional multi-ion mass chromatograms were generated as shown below suggesting overlap of the multiple peaks.

Now, to obtain a high-quality mass spectrum for the compound drawn in red, the mass spectrum (c) was subtracted from one at (b), then the resulting mass spectrum was searched to obtain acetic acid as a candidate with 98% match quality. Similarly, focusing the compound shown in black line, the mass spectrum at (a) was subtracted from one at (c) to obtain a mass spectrum. Then a search was performed on the mass spectrum. Now, benzene was shown as a candidate with 98% match quality.

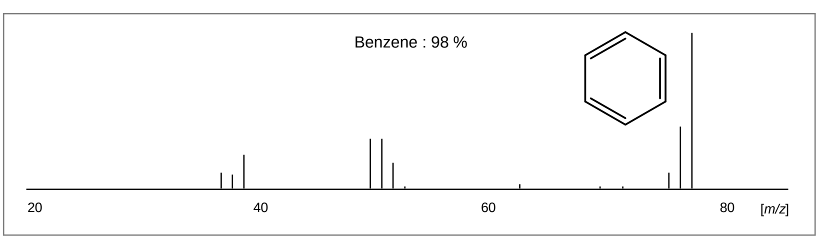




Average mass spectrum from (a) to (c)



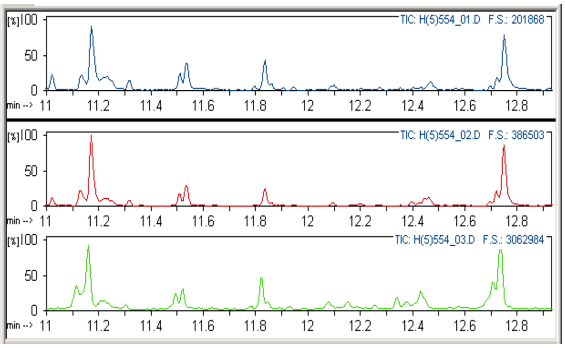
Mass spectrum obtained by subtracting mass spectrum (c) from (b)



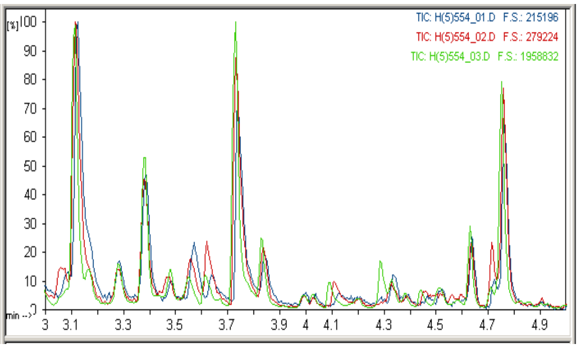
Mass spectrum obtained by subtracting mass spectrum (a) from (c)

5. Overlay of multiple TICs or EICs

Up to a maximum of seven TICs or EICs can be displayed separately or overlaid in the same window.



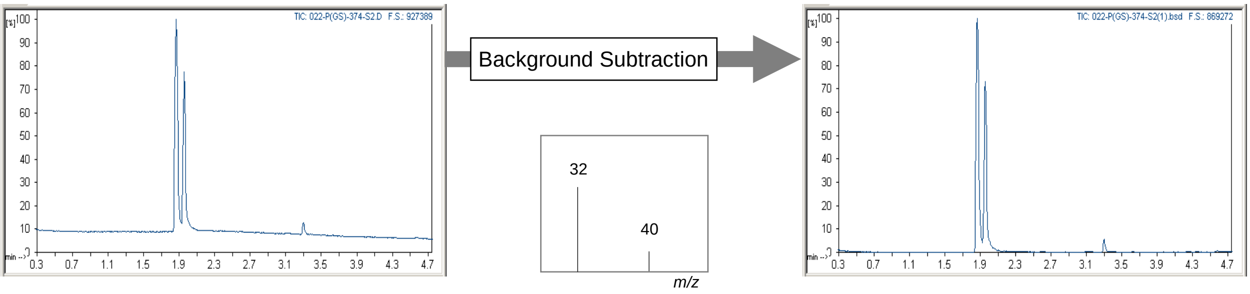
Separate display of TICs



Overlay display of TICs

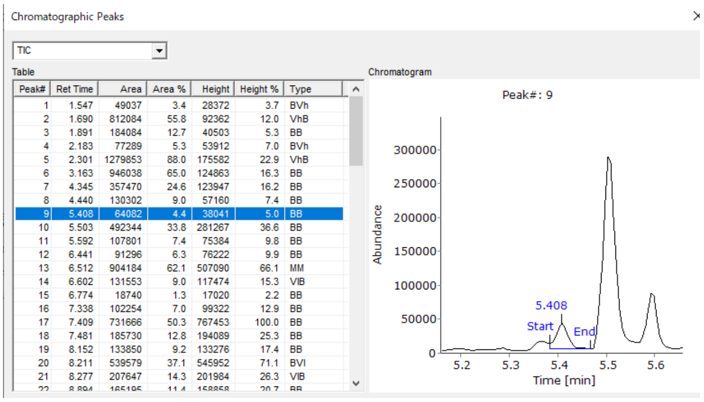
6. Subtracting a mass spectrum from a TIC

A specific mass spectrum can be subtracted from each spectrum in the TIC. This eliminates background or interfering ions from the TIC.



7. Displaying peak area and height

TIC and EIC peaks can be integrated under specified conditions, and the area and height can be displayed. Peak integration lines can be adjusted manually by dragging with the mouse in the detailed view screen.



Peak#	Ret Time	Area	Area %	Height	Height %	Type
1	1.547	49037	3.4	28372	3.7	BVh
2	1.690	812084	55.8	92362	12.0	VhB
3	1.891	184084	12.7	40503	5.3	BB
4	2.183	77289	5.3	53912	7.0	BVh
5	2.301	1279853	88.0	175582	22.9	VhB
6	3.163	946038	65.0	124863	16.3	BB
7	4.345	357470	24.6	123947	16.2	BB
8	4.440	130302	9.0	57160	7.4	BB
9	5.408	64082	4.4	38041	5.0	BB
10	5.503	492344	33.8	281267	36.6	BB
11	5.592	107801	7.4	75384	9.8	BB
12	6.441	91296	6.3	76222	9.9	BB
13	6.512	904184	62.1	507090	66.1	MM
14	6.602	131553	9.0	117474	15.3	VIB
15	6.774	18740	1.3	17020	2.2	BB
16	7.338	102254	7.0	99322	12.9	BB
17	7.409	731666	50.3	767453	100.0	BB
18	7.481	185730	12.8	194089	25.3	BB
19	8.152	133850	9.2	133276	17.4	BB
20	8.211	539579	37.1	545952	71.1	BVI
21	8.277	207647	14.3	201984	26.3	VIB
22	8.894	165195	11.4	158858	20.7	BB

8. Using NIST library directly from within F-Search.

If NIST/EPA/NIH Mass spectral Library (National Institute of Standards and Technology) and its search software have been installed in your PC, you can use it from within F-Search.

Example of an unknown polymer analyzed by EGA-MS and Py-GC/MS

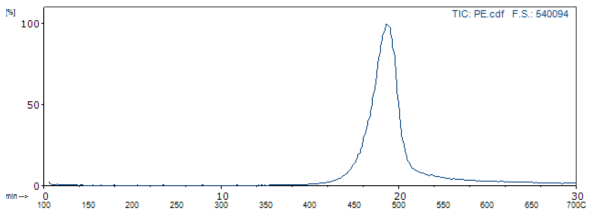
A: Evolved Gas Analysis

(with EGA-MS22B library)

This method allows simple thermal analysis of a sample. The thermogram provides the thermal property of the entire sample.

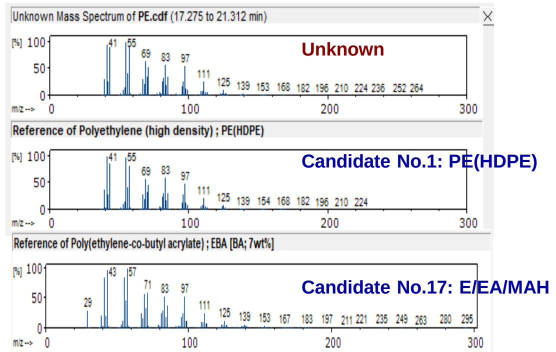
A thermogram obtained using EGA-MS

Furnace temp.: 100 - 600 ºC(20 ºC/min)
ITF Tube: UA-DTM (*L*=2.5 m, i.d.=0.15 mm)
GC Oven: 300 ºC



Searching the EGA-MS22B library

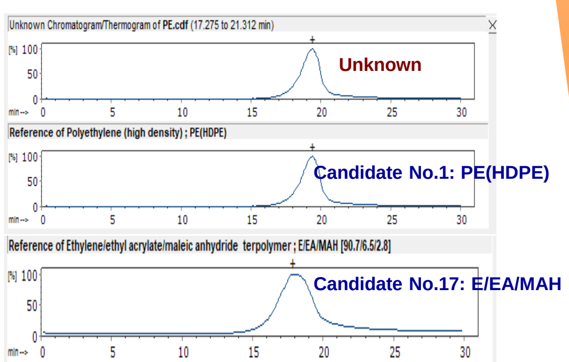
First, the mass spectrum at the apex of the EGA peak of interest is displayed and searched. The unknown sample appears to be PE. However, there are several polymers with match qualities greater than 90%. This suggests that further searches may not be of value.



#	Polymer/Additive	Qual [%]	Start [C]	Top [C]	End [C]	Entry ID
1	PE(HDPE)	99.3	436	486	534	FLT-001
…						
17	E/EA/MAH	97.8	365	455	540	FLK-437
18	L-LDPE	97.7	422	479	550	FLK-031

Comparing the thermogram of the unknown polymer with those of the candidate polymers

Comparing the thermograms of the possible candidates, it shows that candidate No. 17: E/EA/MAH does not match with that of the unknown and can be eliminated from consideration.



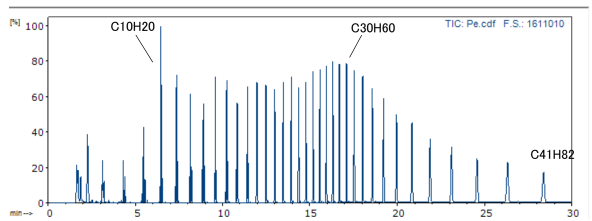
B: Py-GC Analysis

(with PyGC-MS22B library)

This technique offers detailed and advanced analysis of each peak on the pyrogram through analysis of mass spectra.

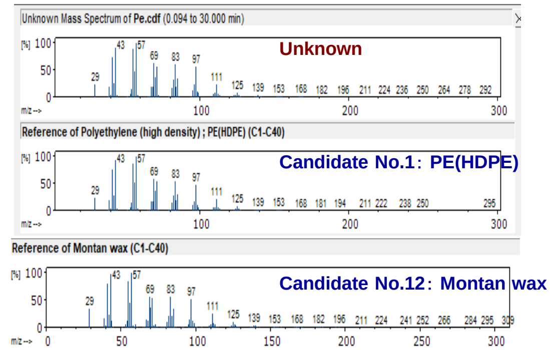
A pyrogram obtained using Py-GC/MS

Furnace temp.: 600 ºC
Col: UA-5(MS/HT) (*L*=30 m, i.d.=0.25 mm, df=0.25 µm)
GC Oven: 40 (2 min) - 320 ºC(20 ºC/min)



Searching the PyGC-MS22B library

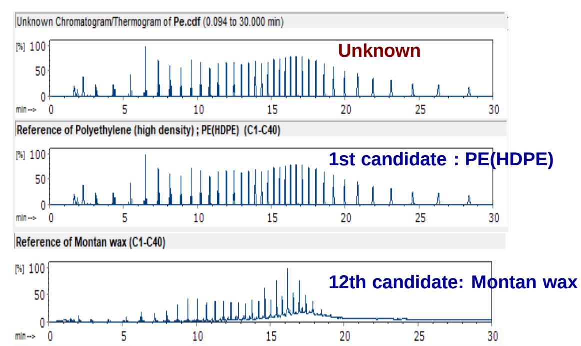
F-Search automatically detects all peaks in the pyrogram and prepares a mass spectrum. This spectrum is then searched. The following results indicate that the unknown polymer is a form of PE. However, there are several polymers with match qualities greater than 90%. This suggests that further searches may not be of value.



#	Polymer/Additive	Qual [%]	Entry ID
1	PE(HDPE)	99.4	FLT-001
…			
12	Montan wax	98.1	FLK-856
13	Oxidized HDPE	97.7	FLK-871

Comparing the pyrogram of the unknown polymer with those of the candidate polymers

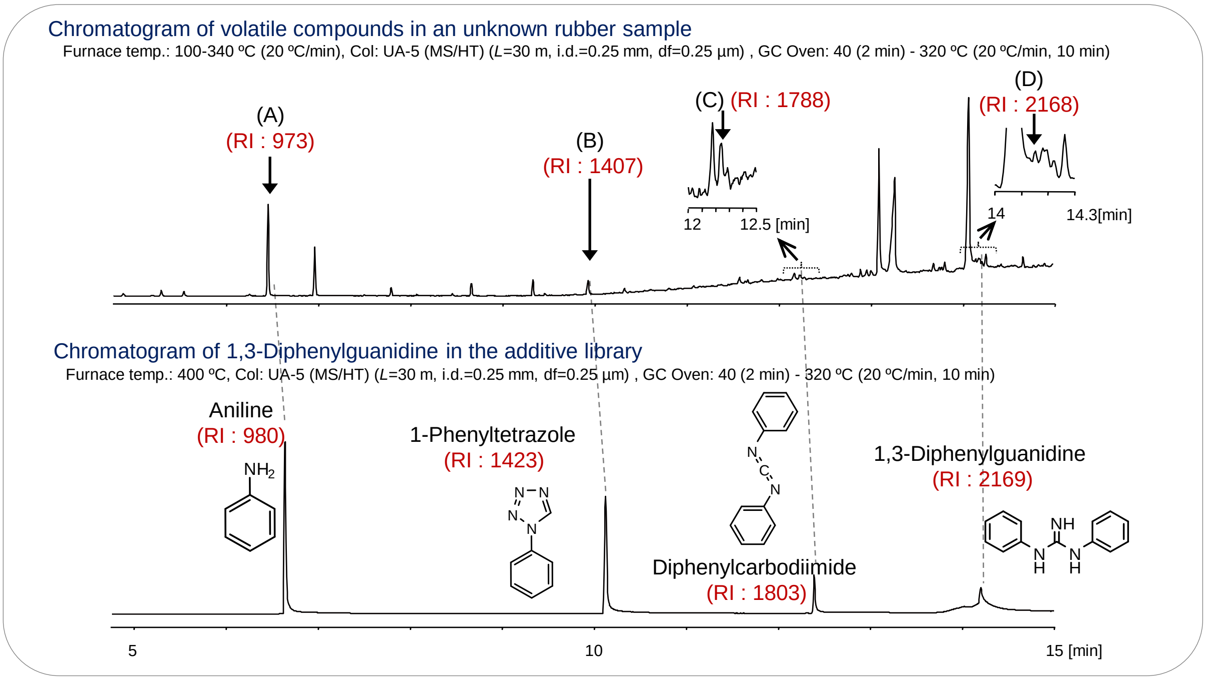
The distribution of the high boiling peaks in the pyrogram of candidate No.12: Montan wax differs from that of the unknown sample and can be eliminated from consideration.



Conclusion : Based on the search results of both thermograms and pyrograms, the unknown sample was narrowed down from the candidate polymers to PE.

Analysis of vulcanization accelerator in rubber (ADD-MS22B library used)

The example below is the analysis of unknown vulcanization accelerator in a compounded rubber sample using TD-GC/MS technique. ADD-MS22B library for additives was searched for peaks (A) - (D) in Fig. 1. They were identified by comparing the mass spectra and the associated retention indexes (RI) to be compounds shown in Fig. 1. In addition, the similarity of the chromatogram for 1,3-Diphenylguanidine to that of the unknown further supports the identification of the vulcanization accelerator.



Search results of peak (D)

	Assignment	Polymer / Additive	Qual [%]	Rt Idx	Rt Time	MW
1	1,3-Diphenylguanidine	1,3-Diphenylguanidine	99.3	2169	14.21	211
2	Aniline	N,N'-Diphenylthiourea	83.1	980	6.64	93
3	Aniline	1,3-Diphenylguanidine	83.1	981	6.64	93
4	Aniline	n-Butylaldehyde-aniline reaction prod...	82.9	980	6.65	93
5	Aniline	Polymerized 2,2,4-trimethyl-1,2-dihyd...	82.0	980	6.76	93

Fig. 1 Library search of volatile compound from rubber sample

Library-search of methyl derivatives of a polymer obtained by thermally assisted hydrolysis and methylation (THM)-GC/MS

(Pyrolyzate-MS22B and PyGC-MS22B libraries used)

An example shown below is the chromatogram of a polymer obtained by THM-GC/MS. A library-search against three peaks in Fig. 2 using F-Search and Pyrolyzate-MS22B library permitted identification of each methyl derivative. The data set stored for each methylated compound includes information of polymer from which it is derived from; therefore, it is very useful. Peak (C) is of unique in this library because it is not in the NIST library.

Using PyGC-MS22B library, a library-search against the mass spectrum obtained by the summation-integration of the mass spectra of three major peaks revealed that the original polymer was found to be poly(ether ether ketone), PEEK.

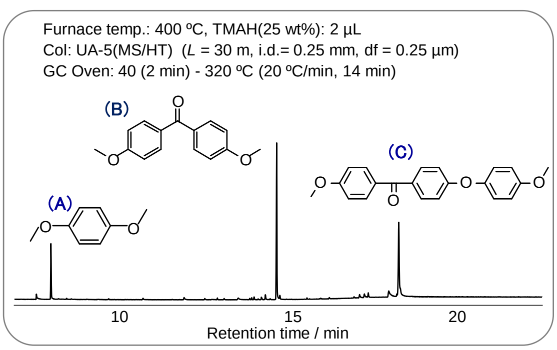


Fig. 2 Library-search of methyl derivatives formed by THM using Pyrolyzate-MS22B library

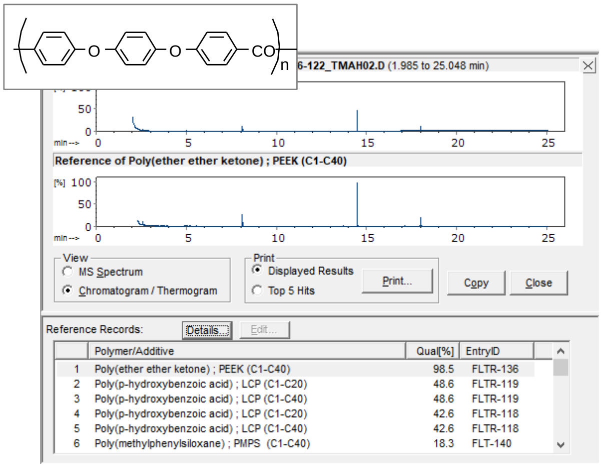


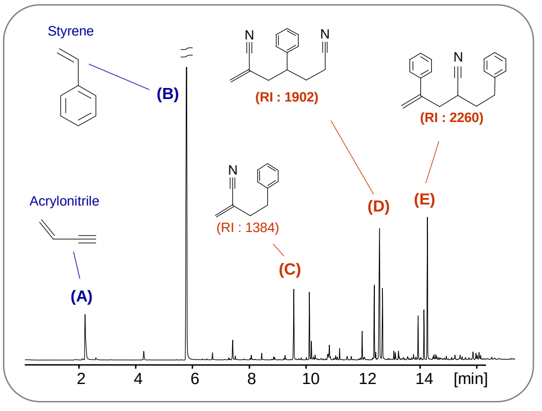
Fig. 3 Polymer search results obtained using integration-summation mass spectrum and PyGC-MS22B library

Polymer search using pyrolyzates of pyrogram (Pyrolyzate-MS22B library used)

Using mass chromatograms, unknown polymers can be identified by searching the polymer library (PyGC-MS22B); however, search can be accomplished utilizing chemical information of pyrolyzates. In the example shown below, an unknown polymer is identified through compound search for each peak. First, from the pyrogram shown in Fig. 4, major peaks (A) through (E) are selected. Then using NIST library, peaks (A) and (B) were identified as acrylonitrile and styrene, respectively; however, there were no candidates for peaks (C) and (D). Using Pyrolyzates MS22B library, peak (E) was identified, and the result is shown in Fig. 4. Candidate polymers can be further narrowed down as shown in Fig. 5.

Pyrogram of unknown polymer

(A) and (B) below were identified by library search on NIST library; however, (C) and (E) could not be identified.

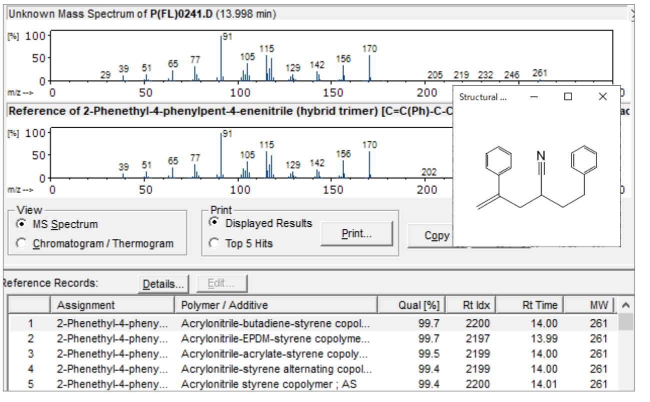


Furnace temp.: 600 ºC, Col: UA-5(MS/HT) (*L*=30 m, i.d.=0.25 mm, df = 0.25 µm), GC Oven: 40 (2 min) - 320 ºC (20 ºC/min)

Fig. 4 Pyrogram of unknown polymer

Search result for peak (E)

Pyrolyzate-MS22B library was searched for the mass spectrum for peak (E), and using the mass spectrum and its retention index (RI), it was estimated to be 2-Phenethyl-4-phenylpent-4-enenitrile. However, there were many polymer candidates of which pyrograms contain the compound. Then candidates must be narrowed down as shown in Fig. D3.



Pyrolyzate candidates generated upon library search.

Polymer candidates which generate 2-Phenethyl-4-phenylpent-4-enenitrile by pyrolysis.

Fig. 5 Search result for peak (E)

Narrowing down from multiple polymer candidates (Visual comparison of pyrograms of polymers stored in the library)

To narrow down candidate polymers, the comparative display capability of F-Search is used. Shown below is the comparison of the pyrograms of candidate polymers obtained in Fig. 6 with the unknown polymer. Candidate 1 can be eliminated by comparing peaks in Group A, and candidate 2 can also be eliminated due to the presence of 1-butene and butanol. Comparing peaks in Group B, the unknown polymer can be narrowed down to be acrylonitrile-EPDM-styrene copolymer through comparison of relative peak heights.

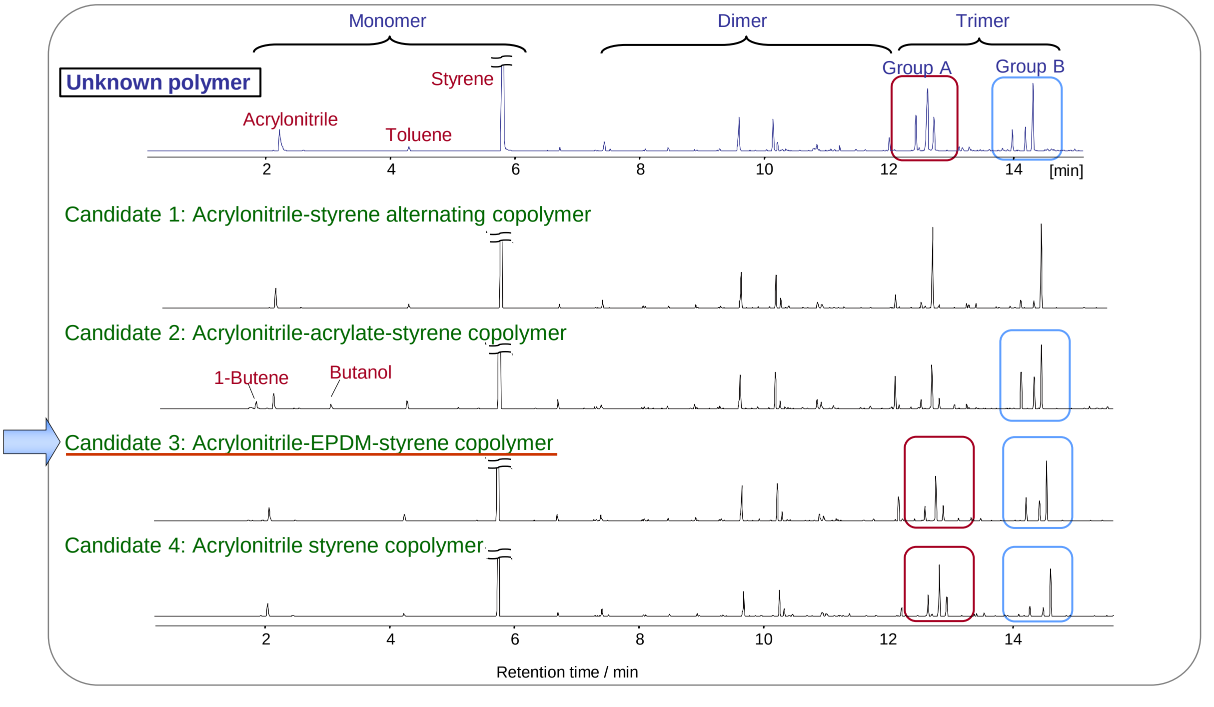
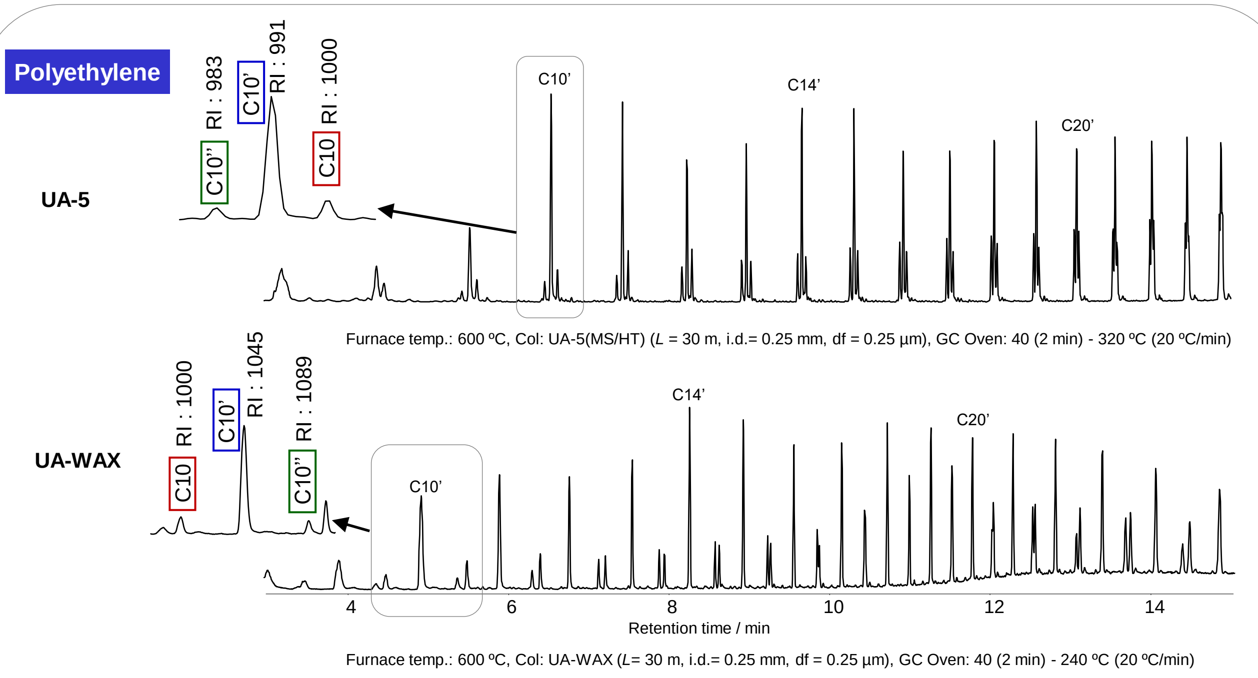


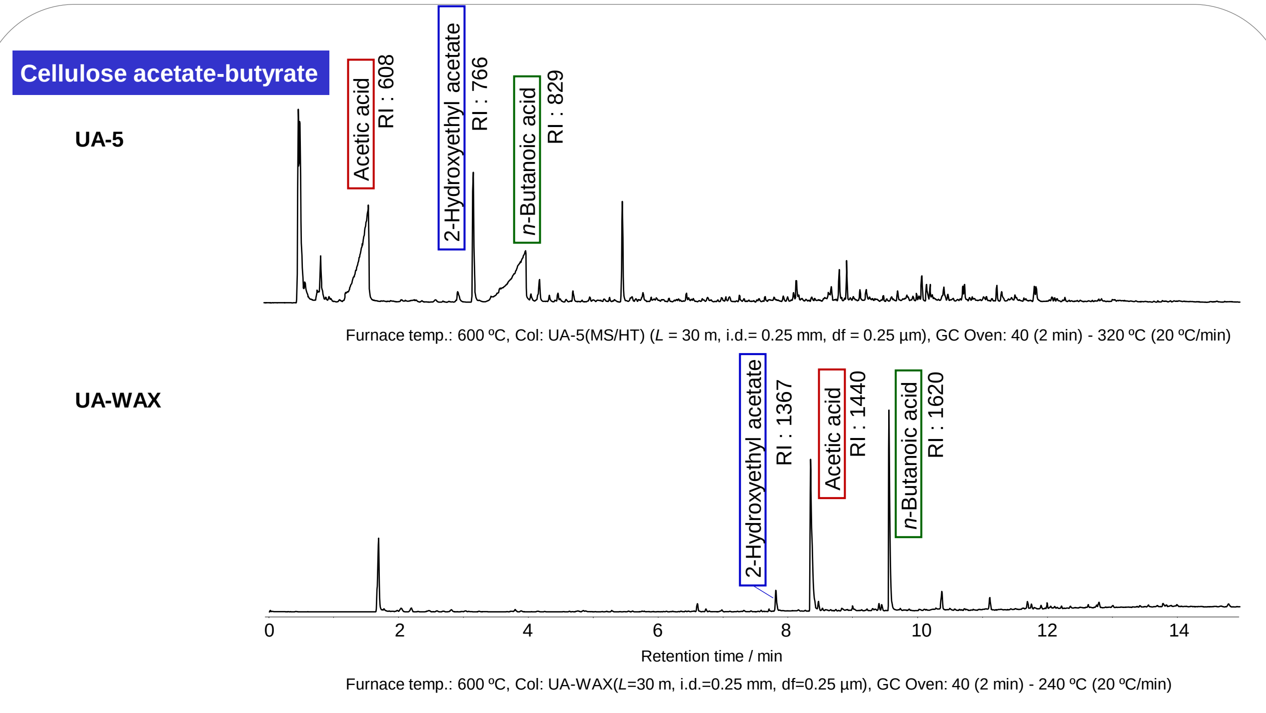
Fig. 6 Visual comparison of pyrograms of polymers stored in the library

UA-5 column and UA-WAX column (Pyrolyzate-MS22B library used)

The low-polarity UA-5 column with 5 % diphenyl – 95 % dimethyl polysiloxane as stationary phase is commonly used for GC/MS analysis. However, free acids and alcohols can cause peak shape deterioration, resulting in leading or tailing peaks. Accordingly, a polar UA-WAX column with polyethylene glycol as stationary phase is used. In ver 3.7, 165 polymers measured using the UA-WAX column have newly been added to the pyrolyzates library. Although the pyrolyzates of polymers are the same as those obtained using the UA-5 column, the elution order of the pyrolyzates differs significantly due to the high polarity of the stationary phase. Therefore, even when the target compounds are overlapping with other compounds in a chromatogram obtained using a UA-5 column, they may be separated with a UA-WAX column. Fig. 7 shows examples of polyethylene and cellulose acetate-butyrate.



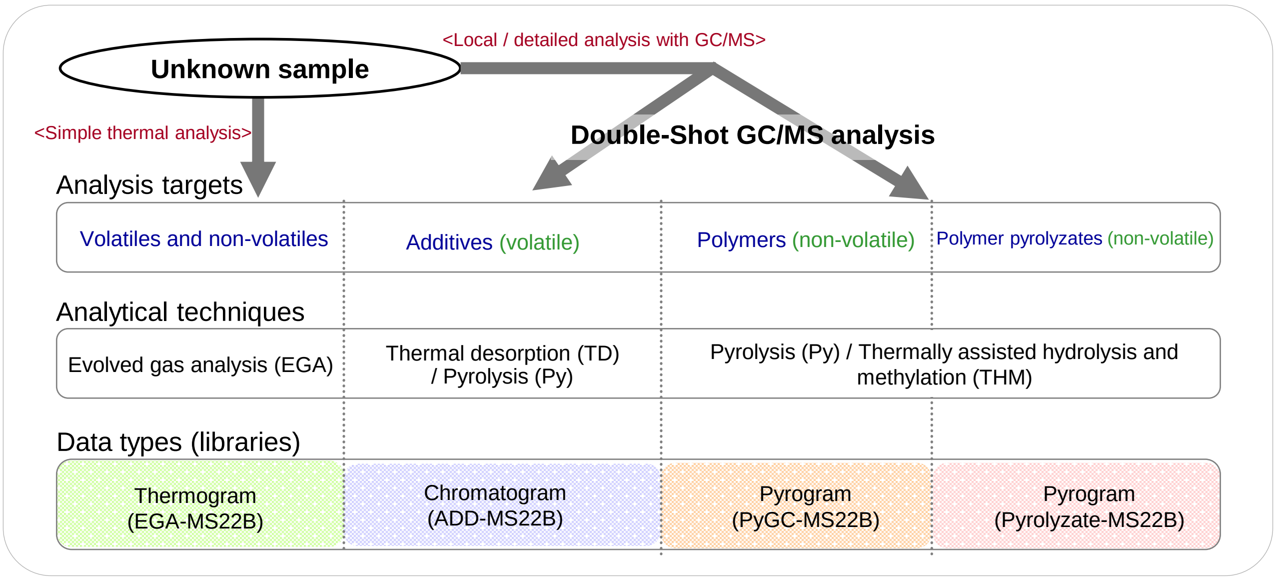
With a UA-5 column, compounds elute in order of boiling point, whereas with a WAX columns, compounds elute in order of polarity, i.e., from low to high polarity. Therefore, the RI of unsaturated hydrocarbons is different.



Carboxylic acids with COOH groups, such as acetic acid and n-butanoic acid, with a UA-5 column give leading peaks due to their low compatibility with the stationary phase. On the other hand, these compounds give sharp peaks with a UA-WAX column.

Fig. 7 Comparison of pyrograms using separation columns of different polarities

Analysis targets, Analytical Techniques, and Libraries for F-Search System



Specifications for F-Search System (Japanese patent 3801355, US patent 6444979)

Product name (P/N)	F-Search "All-In-One" (PY-1110E-221)	Optional libraries (search software F-Search (Ver. 3.7) (PY-1111E-221) required)			
		EGA-MS22B (PY-1112E-221)	**PyGC-MS22B** (PY-1113E-221)	**Pyrolyzate-MS22B** (PY-1115E-221)	**ADD-MS22B** (PY-1114E-221)
Analytical technique	Package contains F-Search (Ver. 3.7) and all four libraries	Evolved gas analysis (EGA-MS)	Pyrolysis-GC/MS (Py-GC/MS) and Thermally assisted hydrolysis and methylation-GC/MS (THM-GC/MS)	Pyrolysis-GC/MS (Py-GC/MS) and Thermally assisted hydrolysis and methylation-GC/MS (THM-GC/MS)	Pyrolysis-GC/MS (Py-GC/MS) and Thermal desorption-GC/MS (TD-GC/MS)
Number of polymers/additives		1,315 polymers	1,315 polymers (THM data in 33 polymers)	268 polymers (containing165 polymer data obtained using UA-WAX column)	590 additives (Py and TD data in 200 additives)
Stored chromatogram		Thermogram	Pyrogram/chromatogram		
Number of mass spectra		c.a. 2,400	c.a. 3,700	c.a. 8,900	c.a. 5,800
Other		Contains all polymers listed in "**Pyrolysis - GC/MS Data Book of Synthetic Polymers -Pyrograms, Thermograms and MS of Pyrolyzates-**" S. Tsuge , H.Ohtani and C. Watanabe, 2011, Elsevier Inc.			Contains 321 additives recorded in "Standard Spectral Database for Polymer Additives '94/95", S. Tsuge, S. Takayama, 1994, Nihon Kagaku Johosha, in addition to 37 major additives for rubbers.
Compatible GC/MS (Available software)		Agilent (MassHunter, ChemStation), Shimadzu (GCMSsolution, LabSolutions), and JEOL (Novaspec, Escrime) Thermo, Varian, PerkinElmer, and LECO require conversion to AIA format.			
PC system required		OS : Windows 11, 10, 8.1 (64 bit or 32 bit) minimum hard disk space 500 MB			

- The complete lists of polymers and additives contained in the libraries are available on Frontier Laboratories' website.
- F-Search can be installed on up to two PCs per single serial number.

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