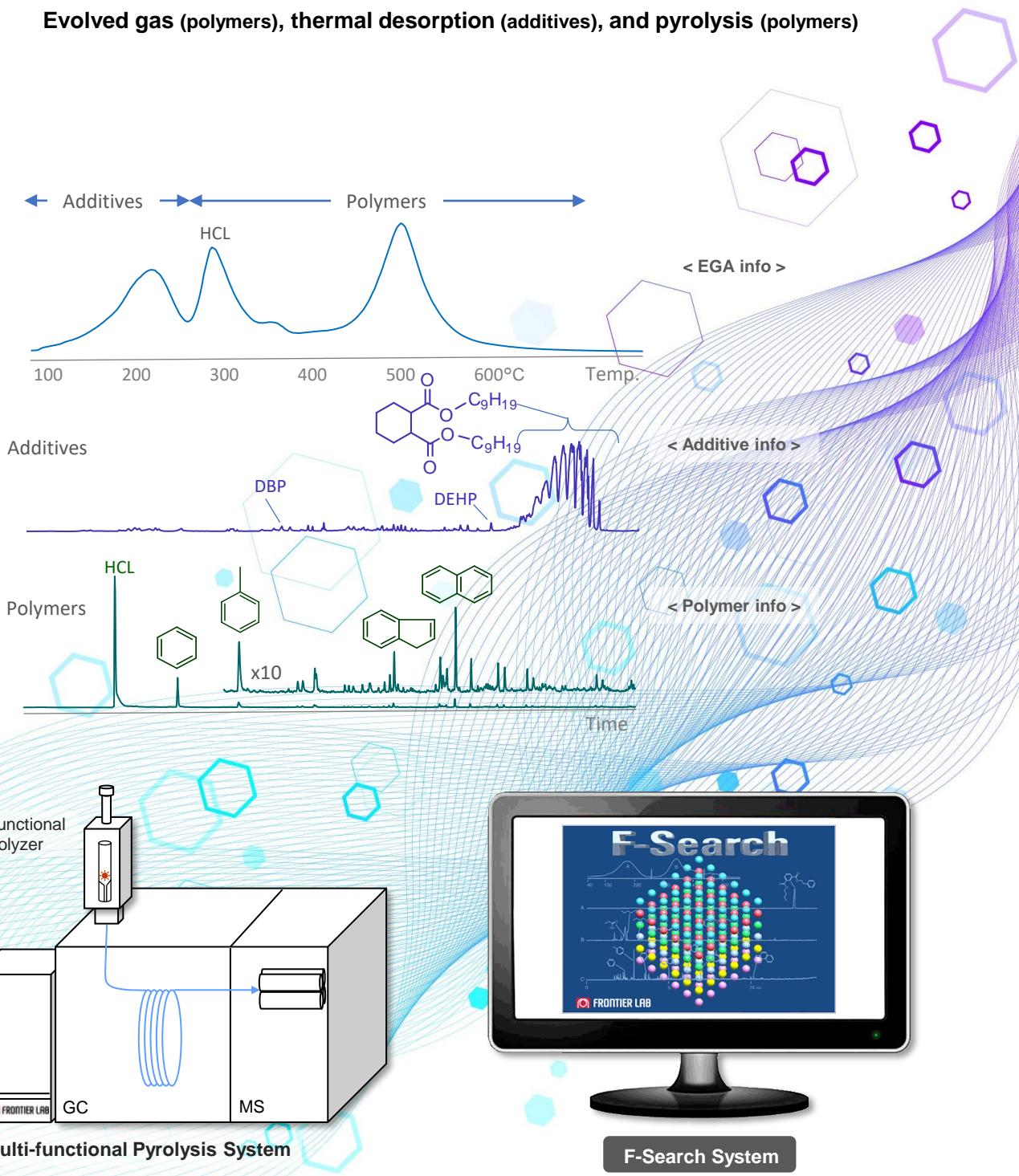


F-Search System

Search software F-Search (Ver. 3.8) that supports polymer analysis, and varied types of libraries:

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



“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. 3.8). Approximately 650 polymers, including natural products, textiles, fats, oils, adhesives, and more, have been newly added. This significantly broadens its applications, making it useful not only for general analysis but also for foreign matter analysis.

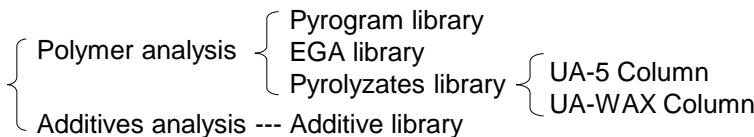
Eight Unique Advantages of F-Search System

(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



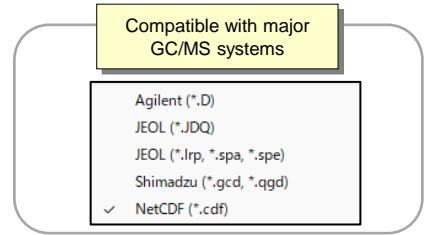
- ADD-MS22B.fl
- EGA-MS24B.fl
- PyGC-MS24B.fl
- Pyrolyzate-UA5-MS22B.fl
- Pyrolyzate-UAWAX-MS22B.fl

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.

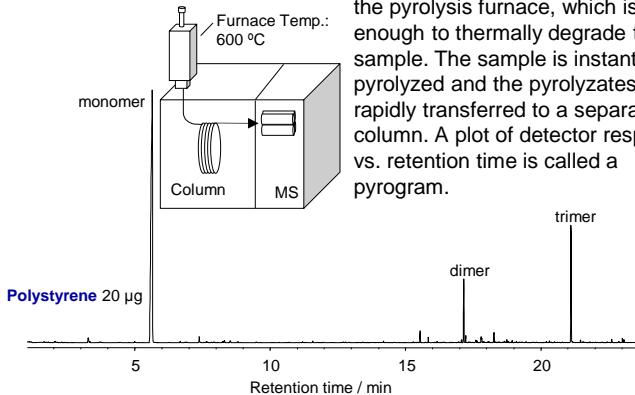
Because the unique search algorithm is used to compare mass spectra, candidate compounds are instantly displayed. Also, the search can be simultaneously performed across multiple libraries.

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.

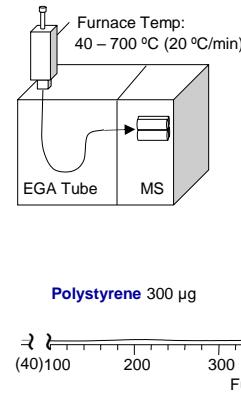


1 : What is Py-GC?

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 °C.

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

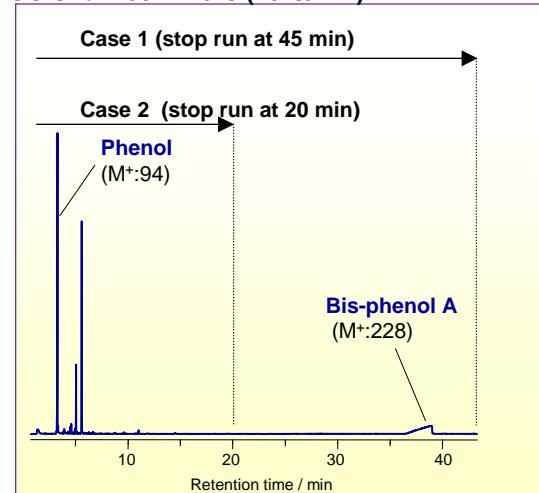
results from Case 1 and Case 2. In both Cases 1 and 2, BT resin was the first candidate. The library contains three sets of mass spectra for the retention times of C1 - C10, C1 - C20, and C1 - C40, so even if a compound with a high boiling point is missing, as in Case 2, equivalent results can be obtained. 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

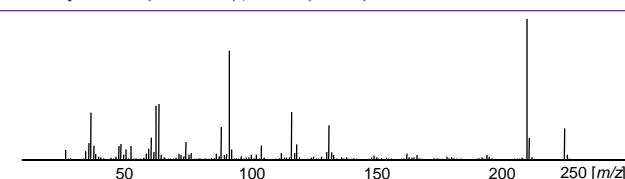
Furnace temp.: 600 °C, Col: UA-5 (MS/HT) ($L=30$ m, i.d.=0.25 mm, df=0.25 μ m)

GC Oven: 60 - 170°C (20°C/min)



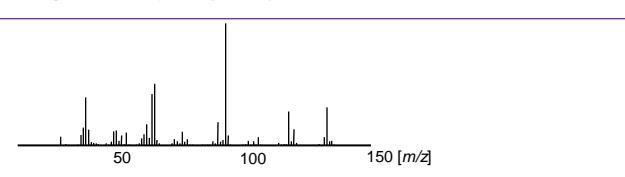
Case 1 (mass spectrum of the peaks detected from 0 to 45 min)

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)

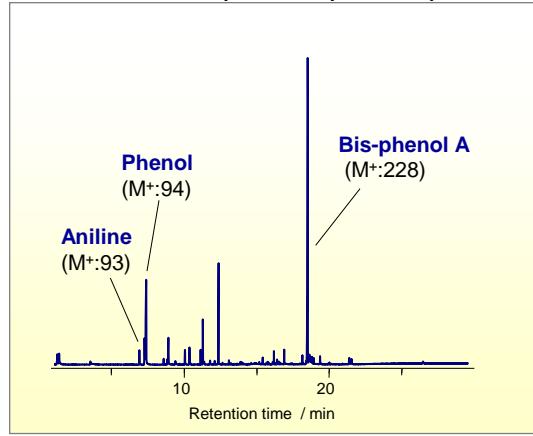
Polymer/Additive	Qual[%]	EntryID
1 Bismaleimide-triazine resin ; BT (C1-C20)	90.2	FLK-338
2 Bismaleimide triazine resin ; BT resin (C1-C20)	83.8	FLT-107
3 Polyetheretherketone ; PEEK (C1-C40)	82.9	FLK-273
4 Polyetheretherketone ; PEEK (C1-C20)	81.9	FLK-273
5 Polyethersulfone ; PESF (C1-C10)	81.9	FLG-705



Data 2

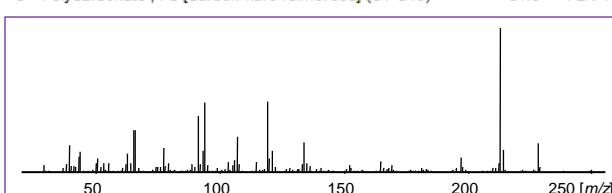
Furnace temp.: 600 °C, Col: UA-5 (MS/HT) ($L=30$ m, i.d.=0.25 mm, df=0.25 μ m)

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



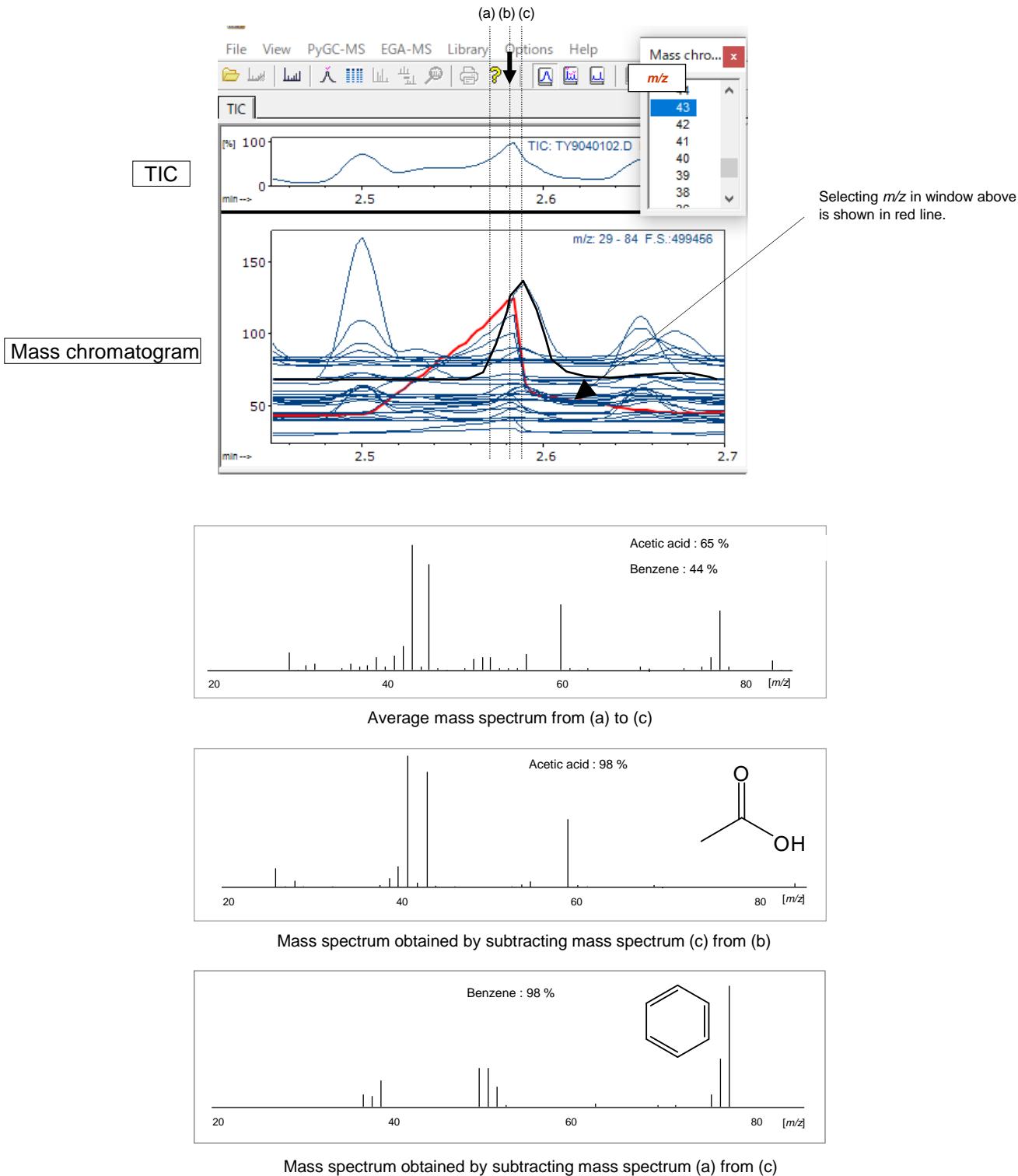
4. Two-dimensional multi-ion chromatograms allow you to obtain high quality mass spectra from overlapping peaks.

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

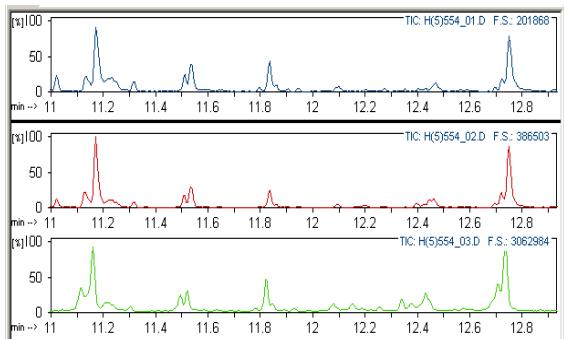
chromatograms were generated as shown below suggesting overlap of the multiple peaks.

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.

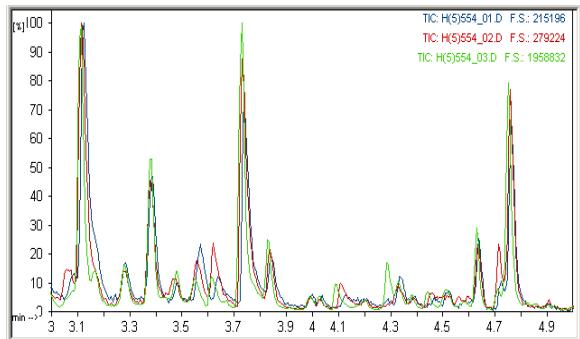


5. Overlay of multiple TICs or EICs

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



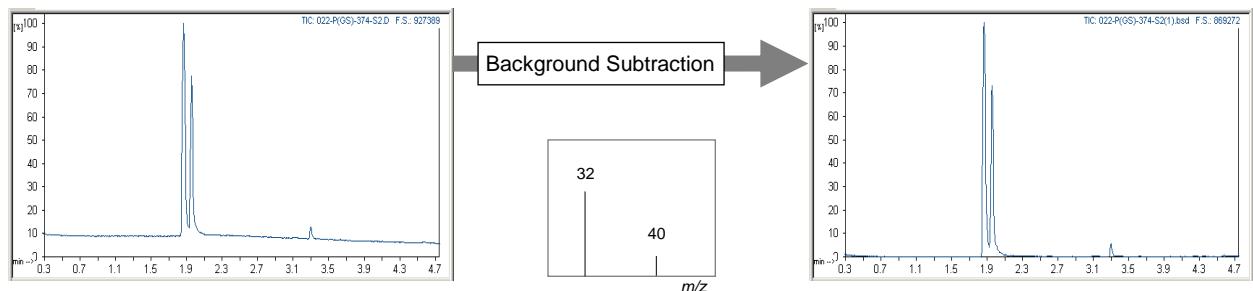
Separate display of TICs



Overlay display of TICs

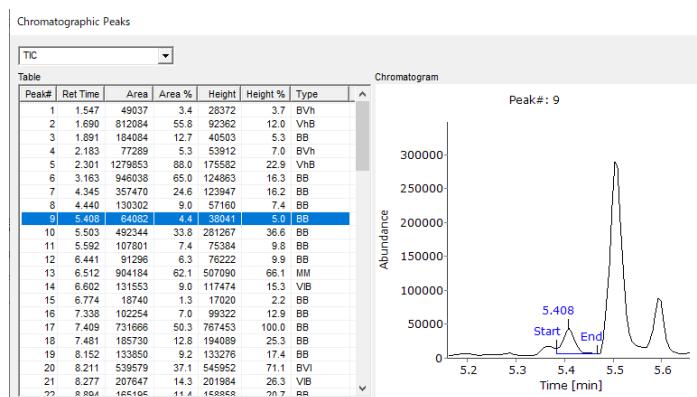
6. Subtracting a mass spectrum from a TIC

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.



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

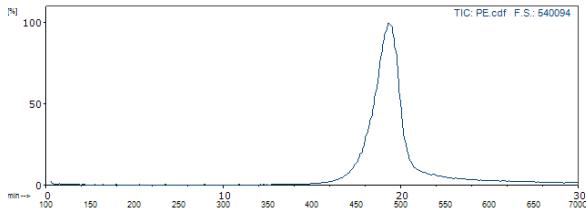
A: Evolved Gas Analysis

(with EGA-MS24B library)

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

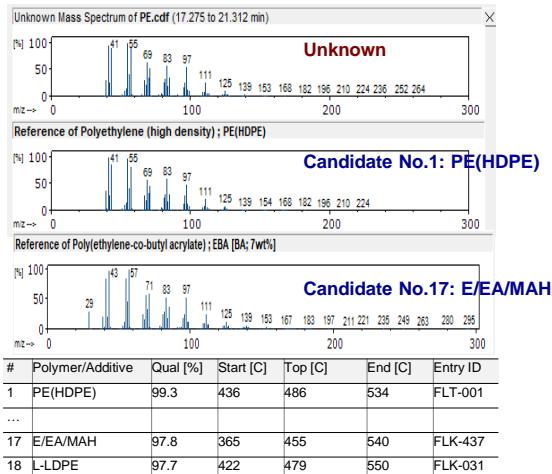
A thermogram obtained using EGA-MS

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



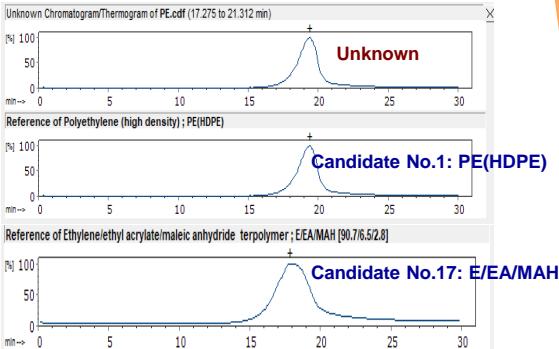
Searching the EGA-MS24B library

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.



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.



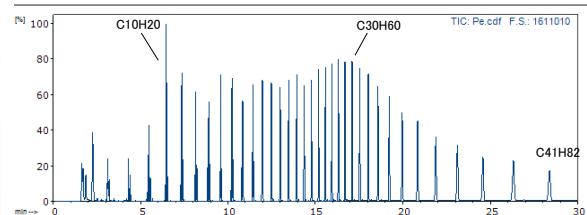
B: Py-GC Analysis

(with PyGC-MS24B library)

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

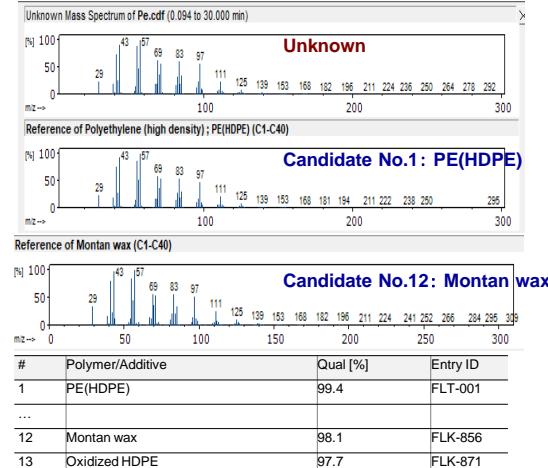
A pyrogram obtained using Py-GC/MS

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



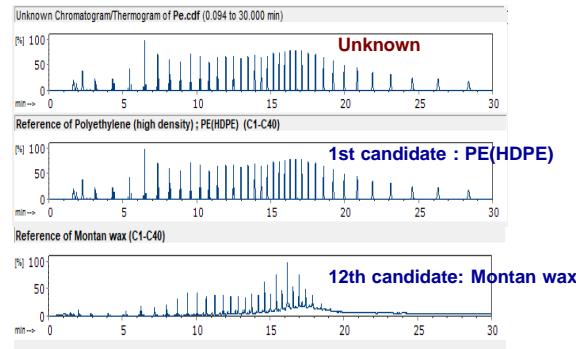
Searching the PyGC-MS24B library

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.



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.

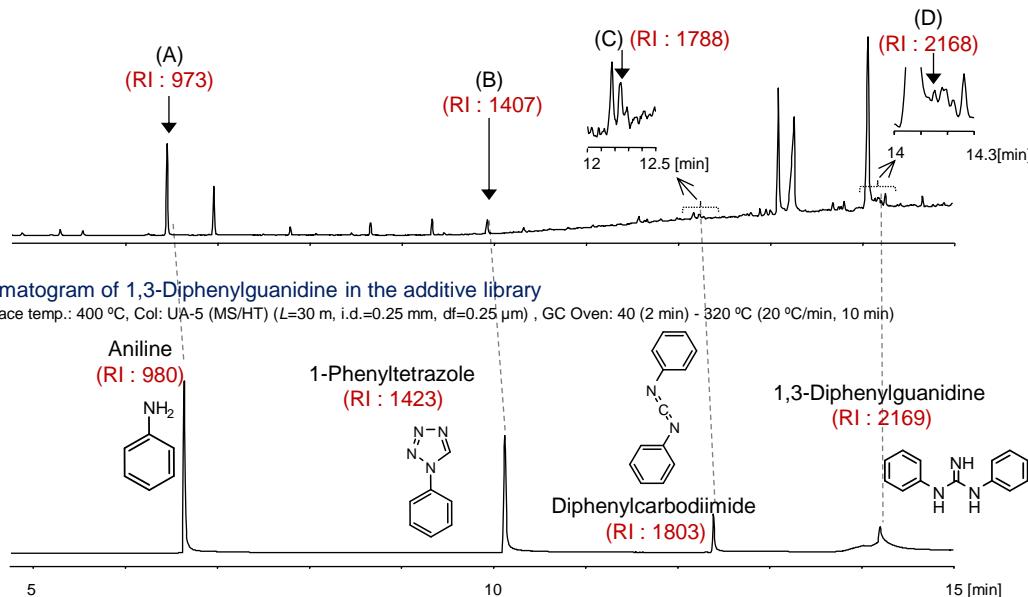
Analysis of vulcanization accelerator in rubber (ADD-MS22B library used)

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.

Chromatogram of volatile compounds in an unknown rubber sample

Furnace temp.: 100-340 °C (20 °C/min), Col: UA-5 (MS/HT) ($L=30$ m, i.d.=0.25 mm, df=0.25 μ m), GC Oven: 40 (2 min) - 320 °C (20 °C/min, 10 min)



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

(Pyrolyze-MS22B and PyGC-MS24B 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 Pyrolyze-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.

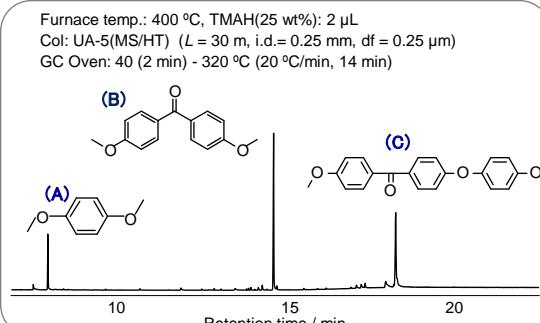


Fig. 2 Library-search of methyl derivatives formed by THM using Pyrolyze-MS22B library

Using PyGC-MS24B library, a library-search against the mass spectrum obtained by the integration-summation of the mass spectra of three major peaks revealed that the original polymer was found to be poly(ether ether ketone), PEEK.

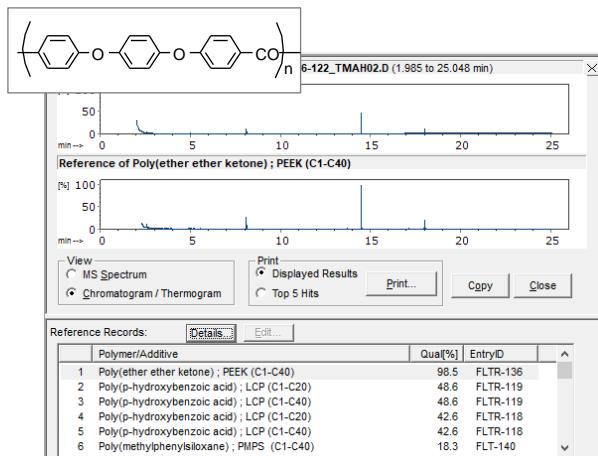


Fig. 3 Polymer search results obtained using integration-summation mass spectrum and PyGC-MS24B library

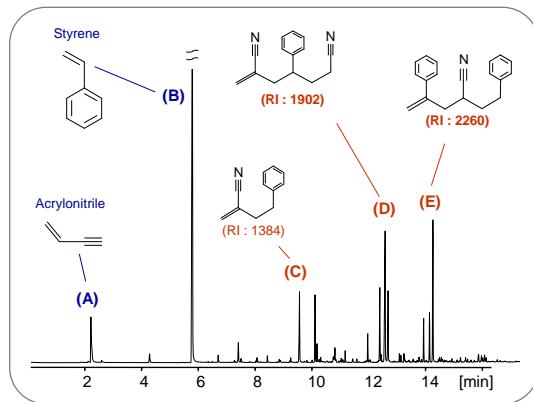
Polymer search using pyrolyzates of pyrogram (Pyrolyze-MS22B library used)

Using mass chromatograms, unknown polymers can be identified by searching the polymer library (PyGC-MS24B); 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.

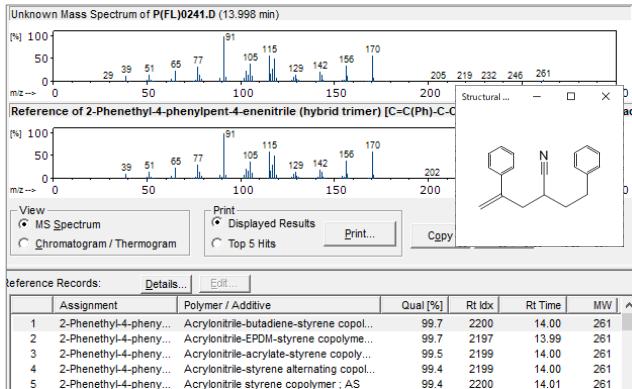


Furnace temp.: 600 °C, Col: UA-5(MS/HT) (L=30 m, i.d.=0.25 mm, df = 0.25 µm), GC Oven: 40 (2 min) - 320 °C (20 °C/min)

Fig. 4 Pyrogram of unknown polymer

Search result for peak (E)

Pyrolyze-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.



Pyrolyze 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.

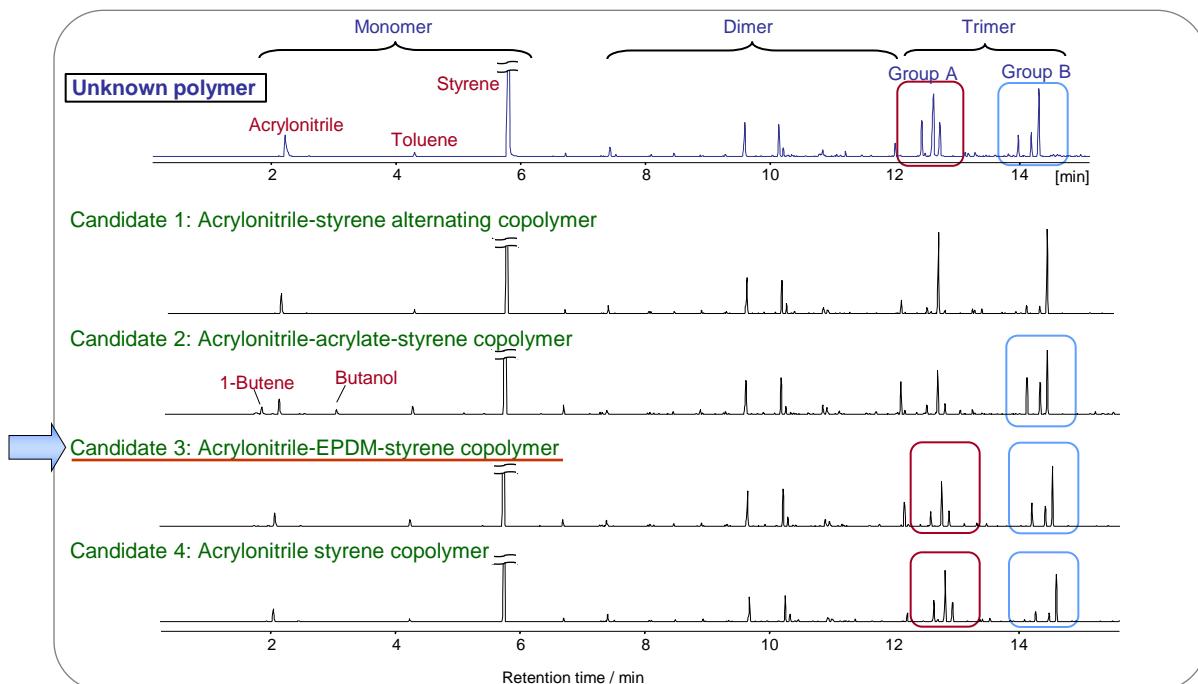


Fig. 6 Visual comparison of pyrograms of polymers stored in the library

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 3.8, the pyrolyzates library contains additional 165 polymers measured using the UA-WAX column. 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-butyrat.

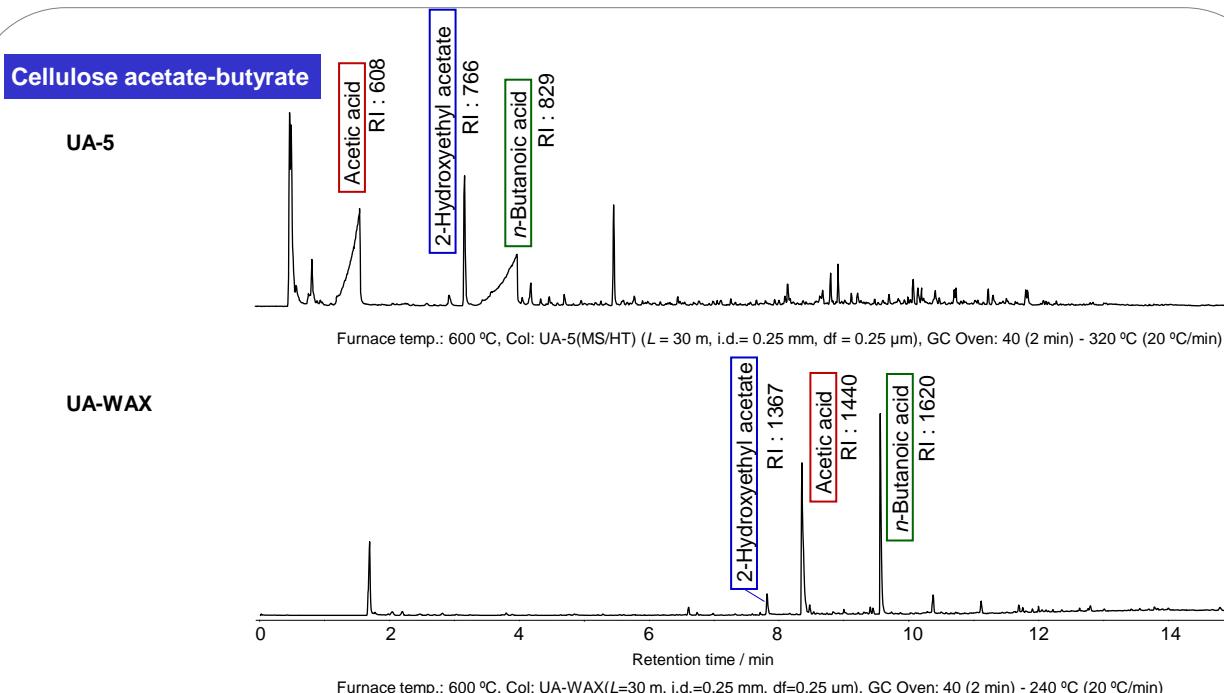
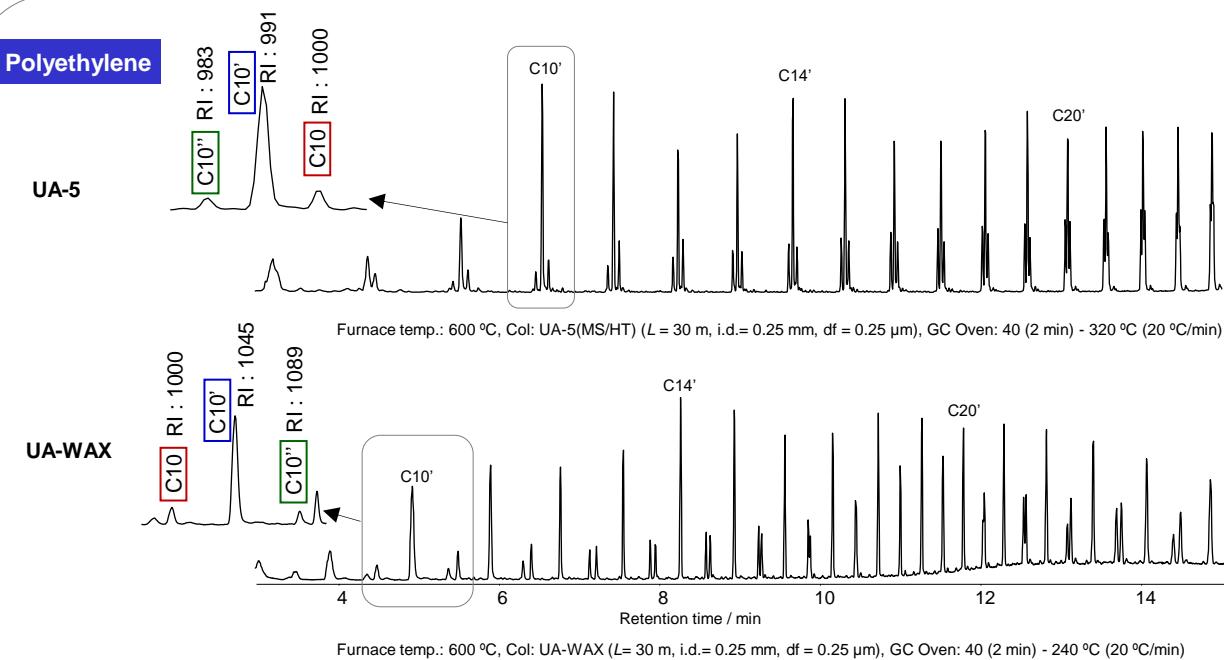
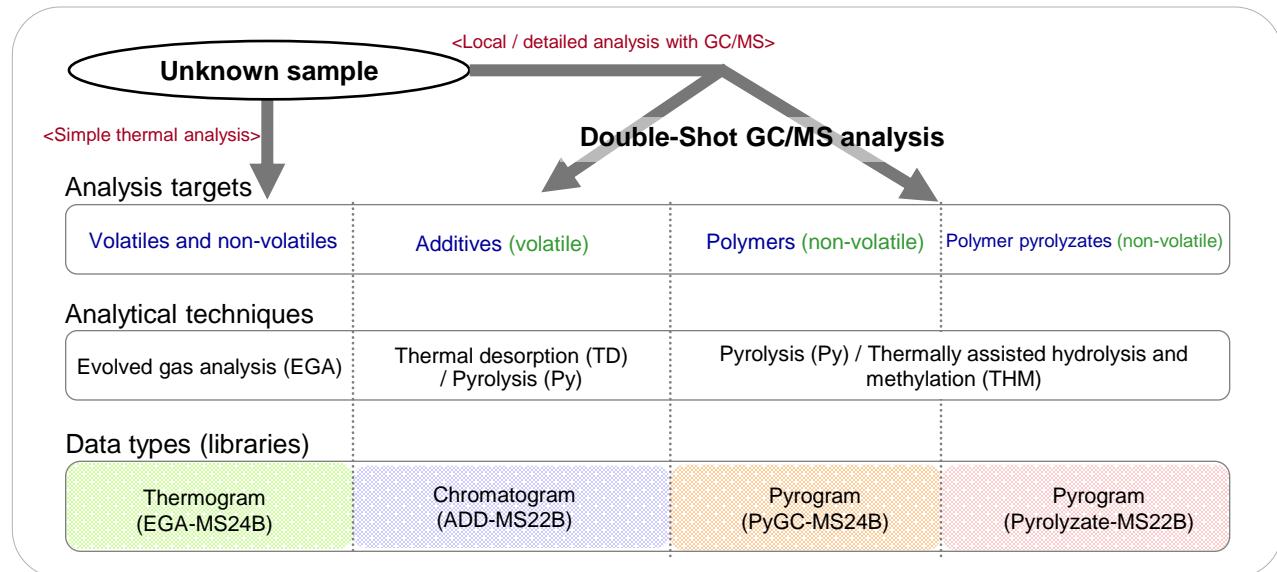


Fig. 7 Comparison of pyrograms using separation columns of different polarities

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-241)	Optional libraries (search software F-Search (Ver. 3.8) (PY-1111E-241) required)			
		EGA-MS24B (PY-1112E-241)	PyGC-MS24B (PY-1113E-241)	Pyrolyzate-MS22B (PY-1115E-221)	ADD-MS22B (PY-1114E-221)
Analytical technique		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		1,960 polymers	1,960 polymers (THM data in 33 polymers)	268 polymers (containing 165 polymer data obtained using UA-WAX column)	590 additives (Py and TD data in 200 additives)
Stored chromatogram	F-Search (Ver. 3.8) and all four libraries	Thermogram	Pyrogram/chromatogram		
Number of mass spectra		c.a. 3,800	c.a. 5,800	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.			
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 storage space : 600 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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