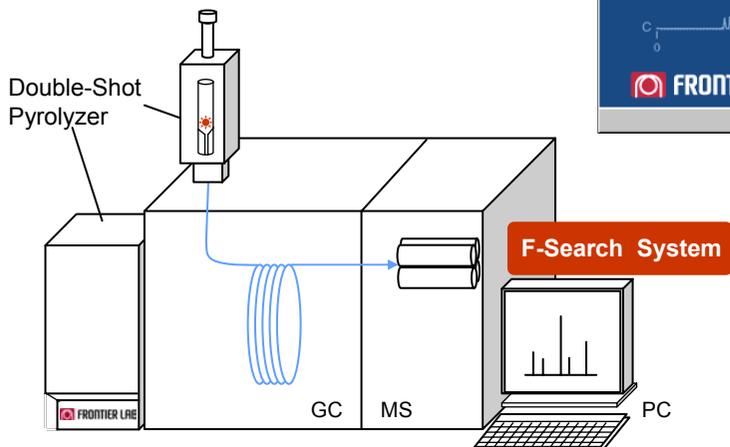
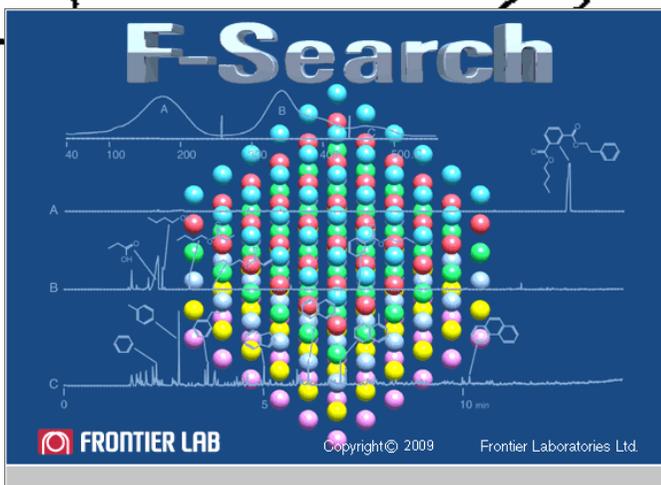


New search software “F-Search (Ver. 3.2)” supports analysis of polymers and additives with a complete list of libraries: pyrograms, thermograms, pyrolyzates, and additives.

# F-Search System



Multi-functional Pyrolysis System (model 2020) and GC/MS

# “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 Double-Shot 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. 3.2) with standard polymer library packages (pyrograms and EGA thermograms) which now contain newly-added 100 polymers in addition to present polymer pyrolyzates library and additives library.

## Seven 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 (Ver. 3.2)

#### ◆ Libraries

- Polymer analysis
  - Pyrogram library
  - EGA library
  - Pyrolyzates library (with chemical structures)
- Additives analysis --- Additive library

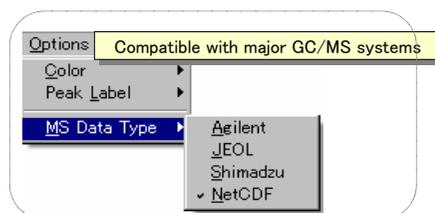
Name	Size	Type
ADD-MS08B.fl	31,179 KB	FL
EGA-MS10B.fl	3,236 KB	FL
PyGC-MS10B.fl	13,924 KB	FL
Pyrolyzate-MS09B.fl	19,717 KB	FL
User-1.fl	1,288 KB	FL

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.

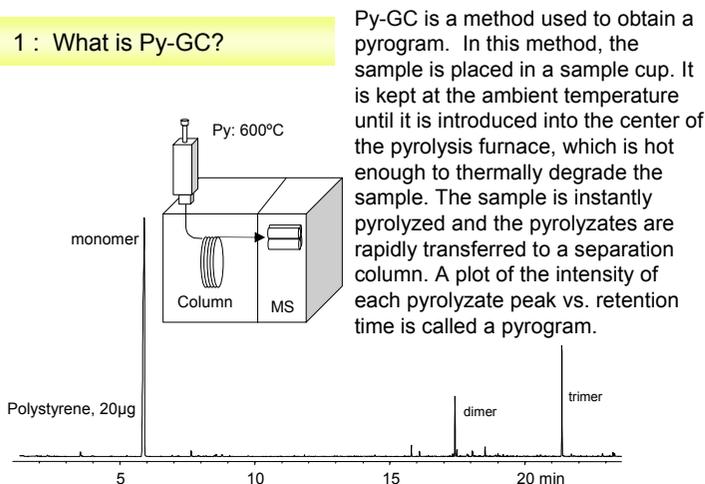
### 2. The search software F-Search (Ver.3.2) allows you to quickly search different types of data such as pyrograms and EGA data. It can also accommodate various GC/MS data formats for your convenience.

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.

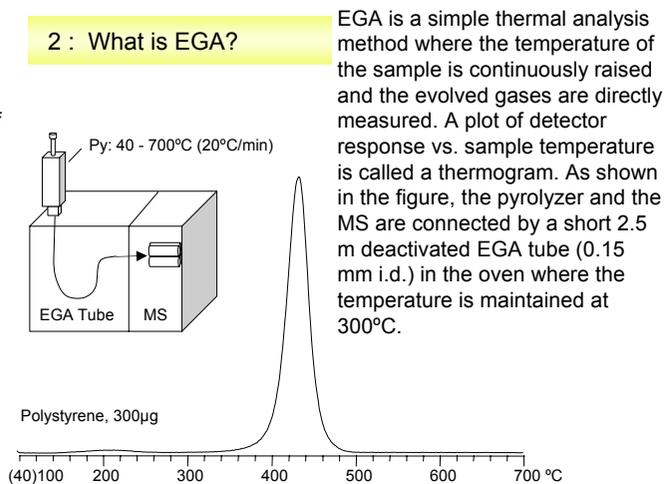
GC/MS data formats of Agilent, Shimadzu, and JEOL can be directly read without any translation or conversion, while other data formats can also be read upon converting to AIA format (NetCDF) files.



#### 1 : What is Py-GC?



#### 2 : What is EGA?



### 3. The unique search algorithm employed in F-Search (Ver. 3.2) is not greatly influenced by the factors such as changes in analytical conditions and separation columns.

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

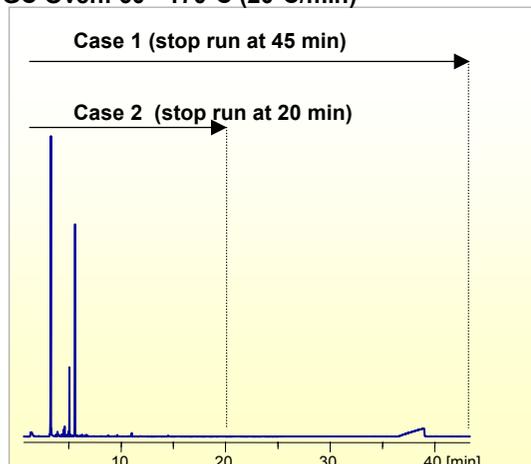
results from Case 1 and Case 2. The Case 1 chromatogram was acquired until 45min; on the other hand, the Case 2 chromatogram was terminated after 20min. The BT resin is the first candidate in Case 1. BT resin-like structures are also nominated as possibilities in Case 2 and BT resin is listed as a candidate with a 76% match quality. This is because the mass spectral database of pyrograms are grouped: C1 through C10, C1 through C20 and C1 through C44. This grouping provides reliable search results independent of the analytical conditions.

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

##### Data 1

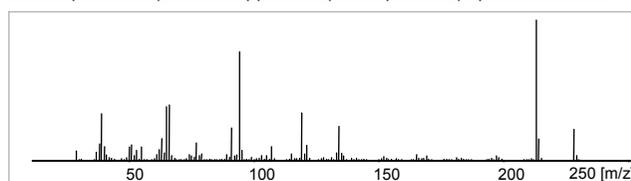
Py Temp.: 600°C, Col: UA-5 (MS/HT) (30 m, 0.25 mm i.d., 0.25 µm)

GC Oven: 60 - 170°C (20°C/min)



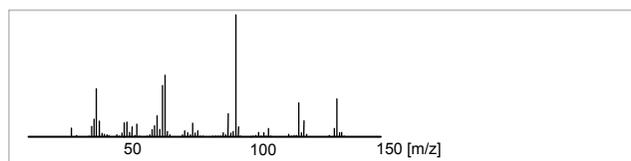
##### Case 1 (mass spectrum of the peaks detected from 0 to 45 min)

	Polymer/Additive	EntryID	Qual[%]
1	<u>Bismaleimide triazine resin ; BT resin (C1-C40)</u>	P(FL)-107	84
2	Polycarbonate (thermally stabilized) (C1-C40)	P(FL)-130	63
3	Polycarbonate(melt method) ; MM-PC (C1-C40)	P(FL)-127	61



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

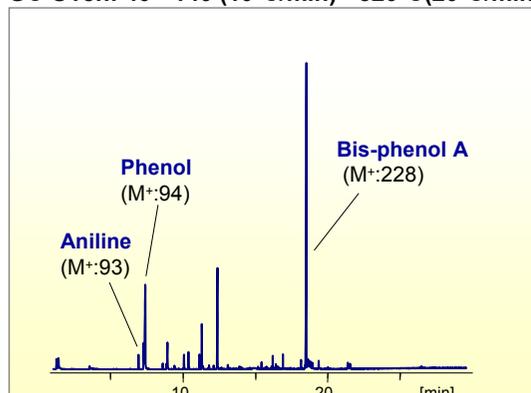
	Polymer/Additive	EntryID	Qual[%]
1	Polycarbonate (solvent method) ; SM-PC (C1-C10)	P(FL)-128	80
2	Polyetherimide ; PEI (C1-C10)	P(FL)-108	79
3	Polyarylate ; PAR (C1-C10)	P(FL)-120	79
⋮			
14	<u>Bismaleimide triazine resin ; BT resin (C1-C20)</u>	P(FL)-107	76



##### Data 2

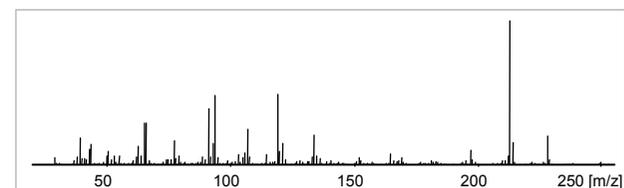
Py Temp.: 600°C, Col: UA-5 (MS/HT) (30 m, 0.25 mm i.d., 0.25 µm)

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



##### Mass spectrum created from all the peaks detected

	Polymer/Additive	EntryID	Qual[%]
1	<u>Bismaleimide triazine resin ; BT resin (C1-C40)</u>	P(FL)-107	94
2	Polycarbonate (thermally stabilized) (C1-C40)	P(FL)-130	78
3	Polycarbonate (solvent method) ; SM-PC (C1-C40)	P(FL)-128	78



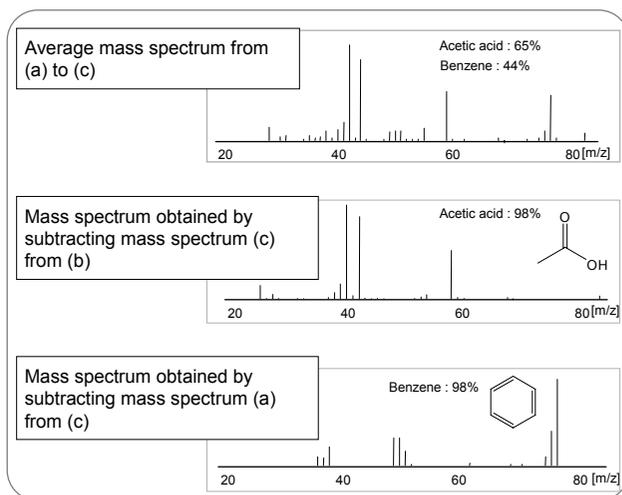
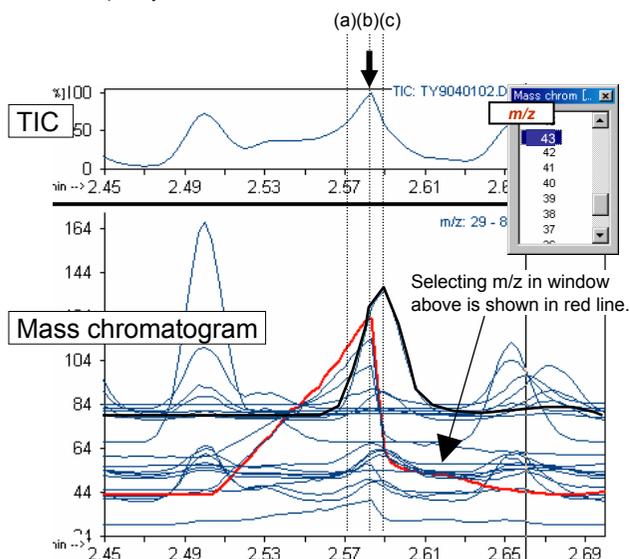
## 4. Two-dimensional multi-ion chromatograms allow you to obtain high quality mass spectra from overlapping peaks.

Pyrograms generally consists of complex pyrolyzates; therefore, it is very important to obtain high quality mass spectra of the targeted peak. F-search (Ver. 3.2) 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 find 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

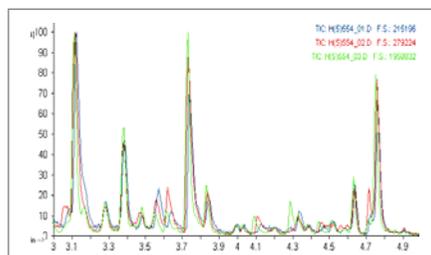
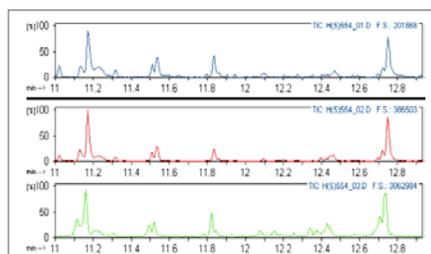
chromatograms were generated as shown below suggesting overlap of the multiple peaks.

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.



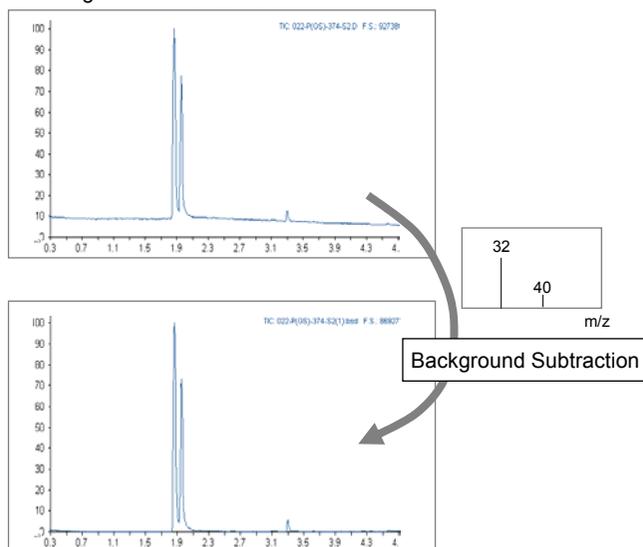
## 5. Overlay of multiple TICs

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



## 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. Now you can search NIST library directly from within F-Search (Ver. 3.2).

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 (Ver. 3.2).

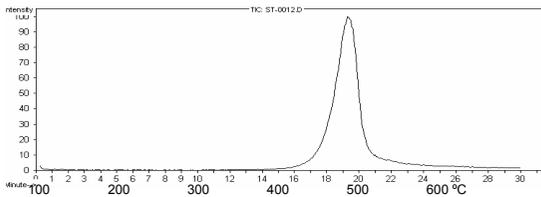
# Example of an unknown polymer analyzed by EGA-MS and Py-GC/MS

## A: Evolved Gas Analysis (with EGA-MS10B library)

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

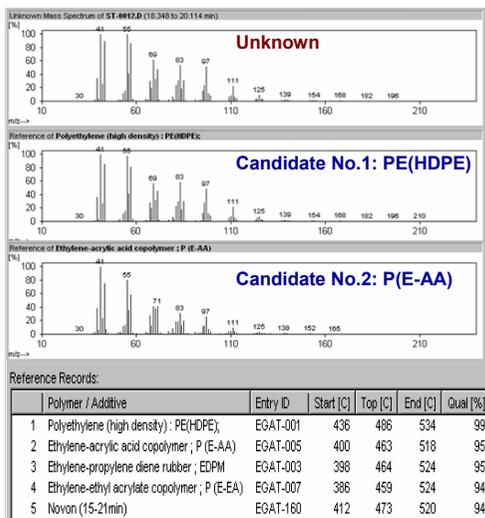
### Obtain a thermogram using EGA-MS

Py Temp.: 100 - 600°C(20°C/min)  
ITF Tube: UADTM (2.5 m, 0.15 mm i.d.)  
GC Oven: 300°C



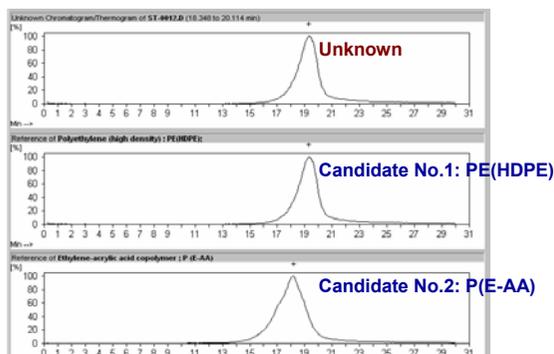
### The search results using the EGA-MS10B library

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, shows that candidate No. 2: P(E-AA) does not match with that of the unknown and can be eliminated from consideration.

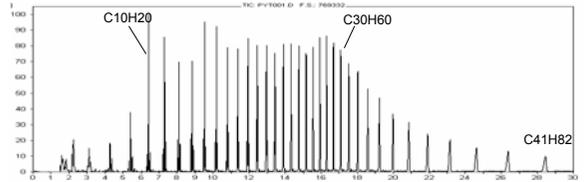


## B: Py-GC Analysis (with PyGC-MS10B library)

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

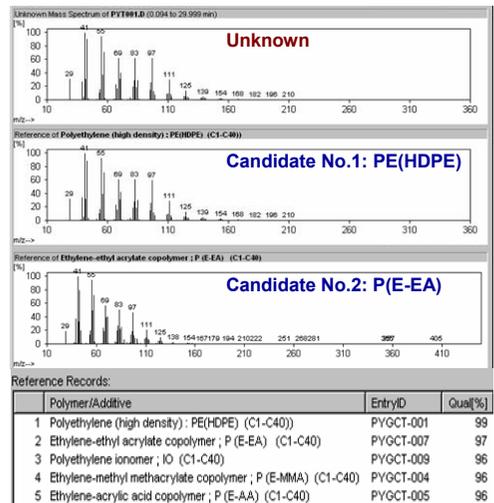
### Obtain a pyrogram using Py-GC/MS

Py Temp.: 600°C  
Col: UA-5(MS/HT) (5% phenylpolydimethylsiloxane, 30 m, 0.25 mm i.d., 0.25 µm)  
GC Oven: 40(2 min) - 300°C(20°C/min)



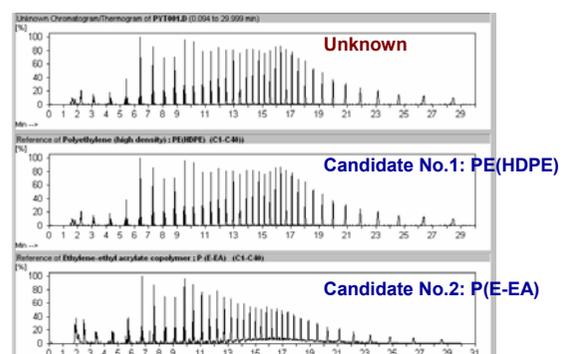
### The search results using the PyGC-MS10B library

F-Search (Ver. 3.2) 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.



### Compare 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.2: P(E-AA) 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 candidates polymers to PE.

## Analysis of additives in “recycled polymer” (ADD-MS08B library is used)

This is a library search example of unknown additives contained in a cell-phone body (polypropylene) using TD-GC/MS technique.

Looking at peak (B) shown in Fig. C1, F-Search (Ver. 3.2) and the additive library (ADD-MS08) were used for a library search. Peaks (A) and (C) were similarly identified.

### Search results for peak (B)

The search results for peak (B) are shown in Fig. C2. From the similarity of the mass spectra and retention indexes(RI), Peak (B) is identified to be an antioxidant: tris(2,4-di-ter-butylphenyl) phosphite.

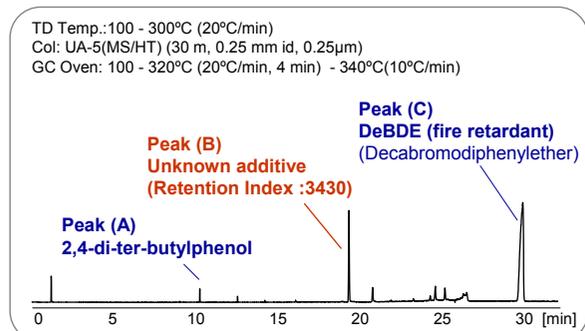


Fig. C1 Chromatogram obtained through TD-GC/MS analysis

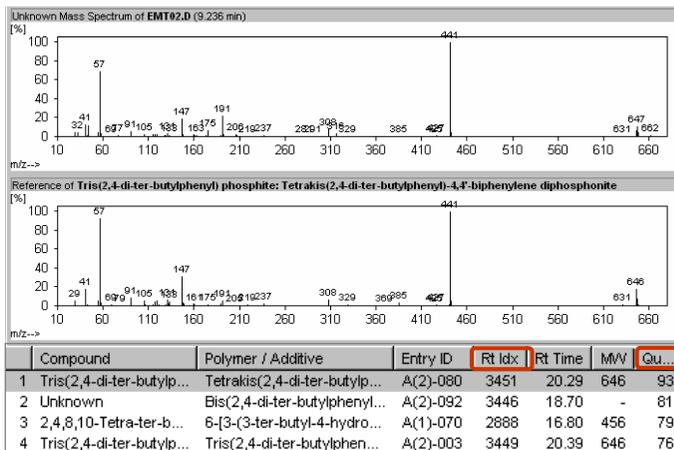


Fig. C2 Search results for peak (B)

## Analysis of antidegradants in rubber (ADD-MS08B library with antidegradants is used)

The example below is the analysis of unknown antidegradants in a compound rubber sample using TD-GC/MS technique. ADD-MS08B library for additives was searched for peaks (A) and (B) in Fig. C3. They were identified by comparing the mass spectra and the associated retention

indexes (RI) to be compounds associated retention indexes (RI) to be compounds shown in Fig. C4. In addition, the similarity of the chromatogram for *p*-(*p*-toluene sulfonylamido) diphenylamine to that of the unknown further supports the identification of the antidegradant.

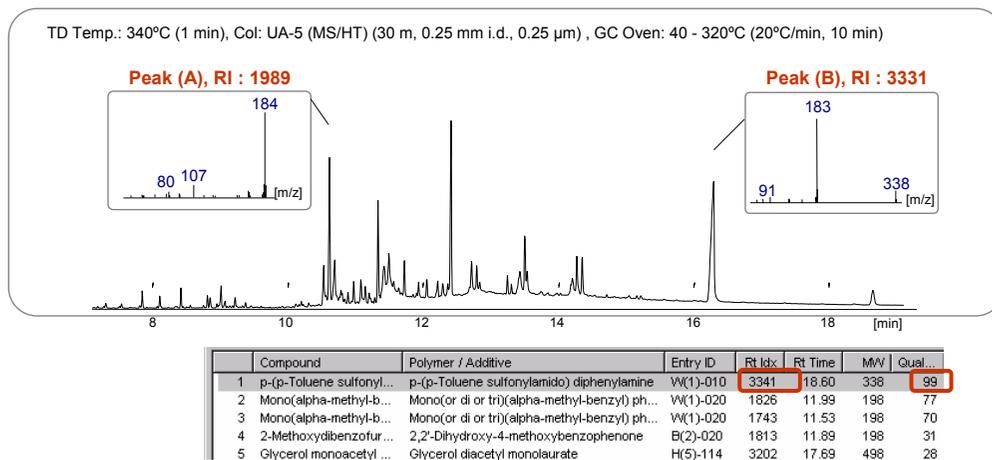


Fig.C3 Chromatogram of volatile in an unknown rubber and search results of peak(B)

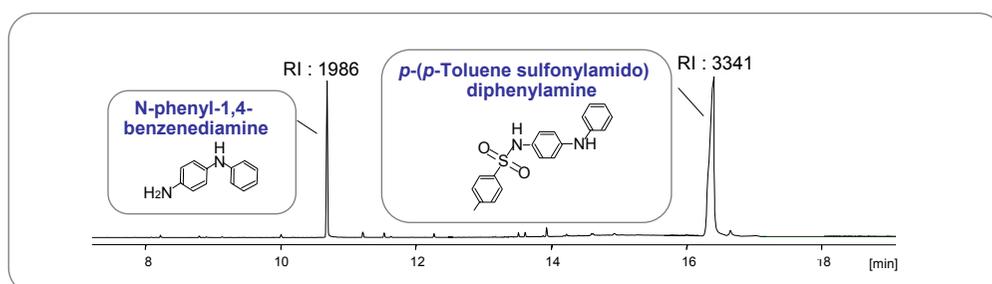


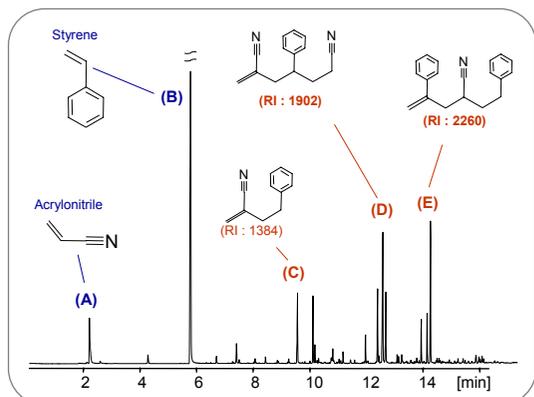
Fig.C4 Chromatogram of *p*-(*p*-Toluene sulfonylamido) diphenylamine in the additive library

# Polymer search using pyrolyzates of pyrogram (Pyrolyzates-MS09B library used)

Using mass chromatograms, unknown polymers can be identified by searching the polymer library (PyGC-MS10B); 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. D1, major

## Pyrogram of unknown polymer

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



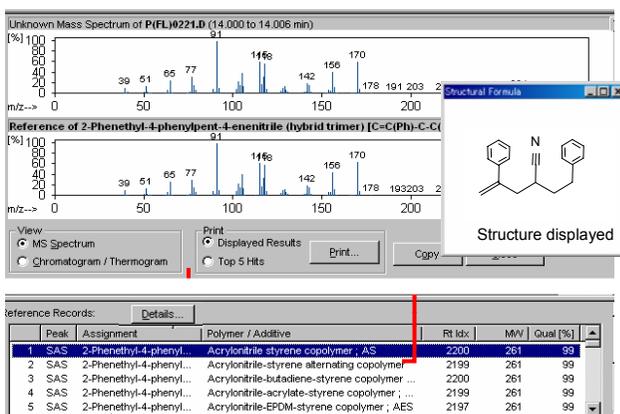
Py Temp.: 600°C, Col: UA-5(MS/HT) 30 m, 0.25  $\Phi$ , 0.25  $\mu$ m  
GC Oven: 40 (2 min) - 300°C(20°C/min)

Fig. D1 Pyrogram of unknown polymer

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 MS09B library, peak (E) was identified and the result is shown in Fig. D2. Candidate polymers can be further narrowed down as shown in Fig. D3.

## Search result for peak (E)

Pyrolyzate-MS09B 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-enitrile. 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-enitrile by pyrolysis.

Fig. D2 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 (Ver. 3.2) is used. Shown below is the comparison of the pyrograms of candidate polymers obtained in Fig. D2 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.

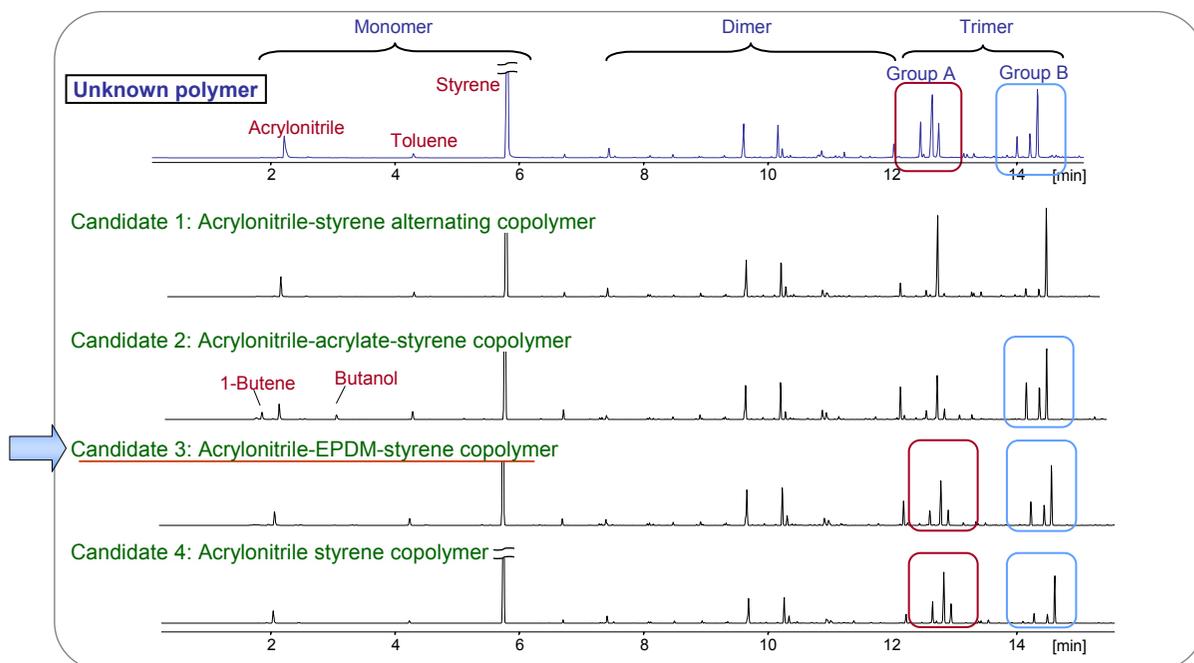
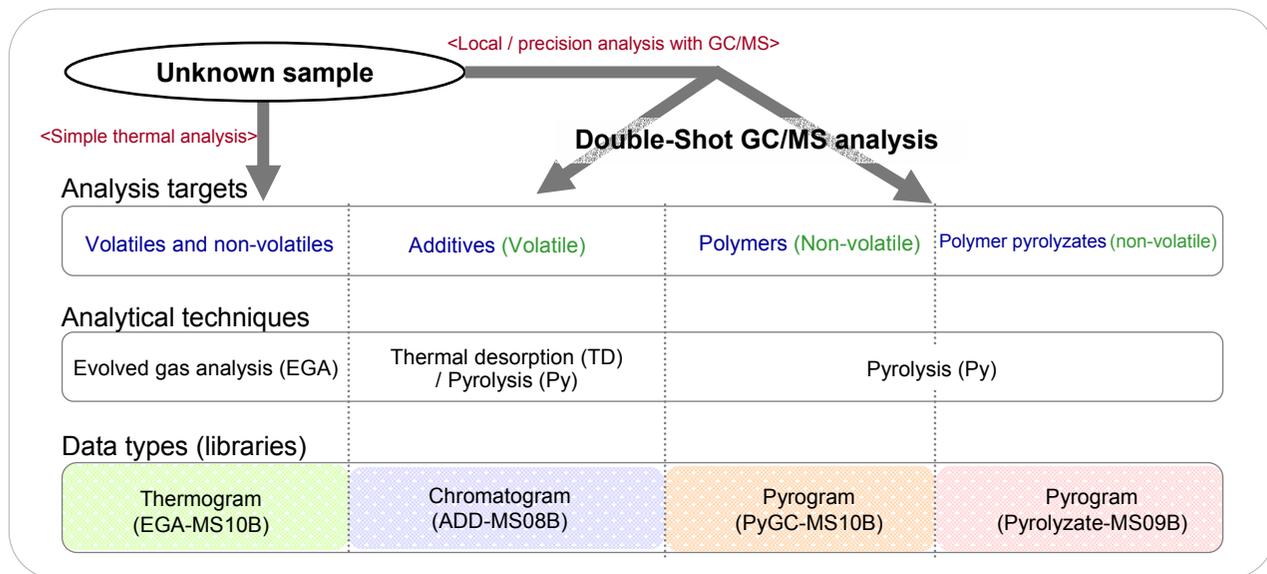


Fig. D3 Visual comparison of pyrograms of polymers stored in the library

# 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-101)	Optional libraries (search software F-Search (Ver. 3.2) (PY-1111E-101) required)			
		EGA-MS10B (PY-1112E-101)	PyGC-MS10B (PY-1113E-101)	Pyrolyzate-MS09B (PY-1115E)	ADD-MS08B (PY-1114E)
Analytical technique	Package contains F-Search(Ver. 3.2) and all four libraries	Evolved gas analysis (EGA-MS)	Pyrolysis-GC/MS (Py-GC/MS)	Pyrolysis-GC/MS (Py-GC/MS)	Pyrolysis-GC/MS (Py-GC/MS) and Thermal desorption-GC/MS (TD-GC/MS)
Number of polymers/additives		268 polymers		165 polymers	358 additives
Stored chromatogram		Thermogram	Pyrogram		
Number of mass spectra		c.a. 500	c.a. 800	c.a. 3,000	c.a. 3,000
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 319 additives recorded in "Standard Spectral Database for Polymer Additives '94/95", S. Tsuge, S. Takayama, 1994, Nihon Kagaku Johosha
Compatible GC/MS		Compatible with all major GC/MS systems. (Data formats used in Agilent, Shimadzu, and JOEL can directly be read. Thermo, Varian, Perkin Elmer, LECO require conversion to AIA format. )			
PC system required		OS : Windows 7, Vista, XP, 2000, 98, NT4.0, hard disk space of max 130MB			

- The complete list of polymers and additives contained in the libraries are available on Frontier Laboratories' website: [www.frontier-lab.com](http://www.frontier-lab.com).



R&D and manufactured by:  
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 Phone: 81-24-935-5100 Fax: 81-24-935-5102