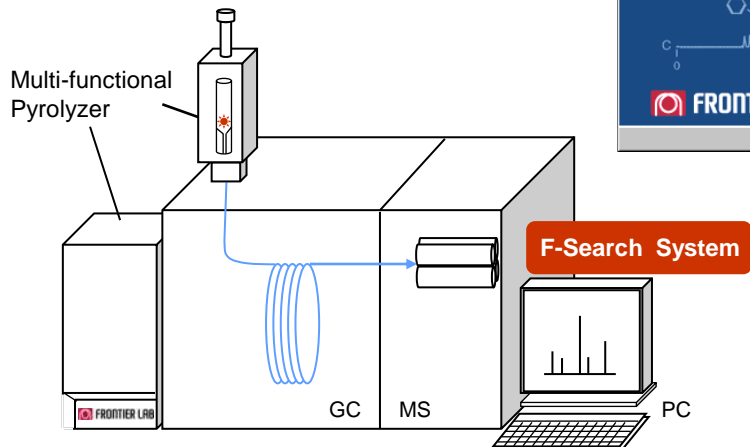New search software "F-Search (Ver. 3.6)" supports analysis of polymers and additives with a complete list of libraries: pyrograms, THM pyrograms, thermograms, pyrolyzates, THM pyrolyzates, and additives.

F-Search System

Multi-functional Pyrolyzer

F-Search System

GC   MS   PC

Multi-functional Pyrolysis System 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 Multi-functional pyrolyzer that allows you to use techniques such as Py-GC, thermal desorption (TD)-GC and evolved gas analysis (EGA).
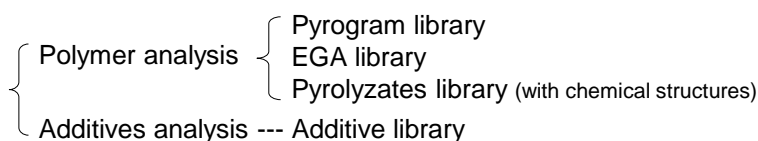
However, interpretation of the pyrogram or EGA thermogram is a difficult task, requiring professional intuition and experience. Frontier Laboratories has now upgraded F-Search (Ver. 3.6). Also, 300 polymers have been newly added to the polymer libraries for a total of 1,000 polymers. Further, the Additive library contains approximately 500 additives and Pyrolyzates library provides pyrolyzates information of 268 polymers.

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.
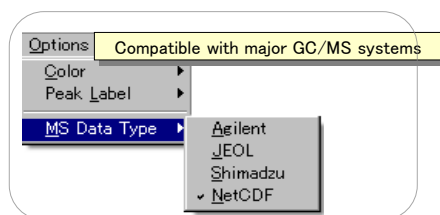
♦ **Search software: F-Search** (Ver. 3.6)

♦ **Libraries**

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

Additives analysis --- Additive library

Name	Size	Type
ADD-MS16B.fl	31,179 KB	FL
EGA-MS18B.fl	3,236 KB	FL
PyGC-MS18B.fl	13,924 KB	FL
Pyrolyzate-MS18B.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.
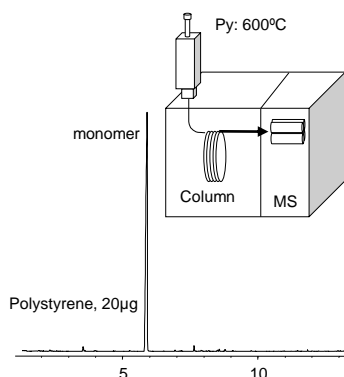
2. The search software F-Search (Ver.3.6) allows you to quickly search different types of data such as pyrograms and EGA data. It can also accommodate various GC/MS data formats for your convenience.

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.
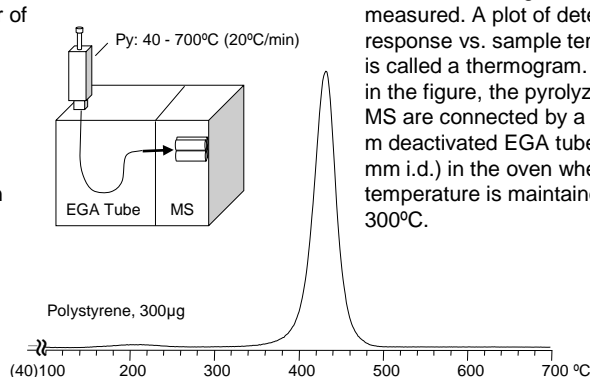
Options
Compatible with major GC/MS systems
Color
Peak Label
MS Data Type
Agilent
JEOL
Shimadzu
✓ NetCDF

---

1 : What is Py-GC?

Py: 600ºC

monomer

Column   MS

Polystyrene, 20µg

dimer   trimer

5   10   15   20 min

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 the intensity of each pyrolyzate peak vs. retention time is called a pyrogram.

2 : What is EGA?

Py: 40 - 700ºC (20ºC/min)

EGA Tube   MS

Polystyrene, 300µg

(40)100   200   300   400   500   600   700 ºC

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 300ºC.

3. The unique search algorithm employed in F-Search (Ver. 3.6) 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 i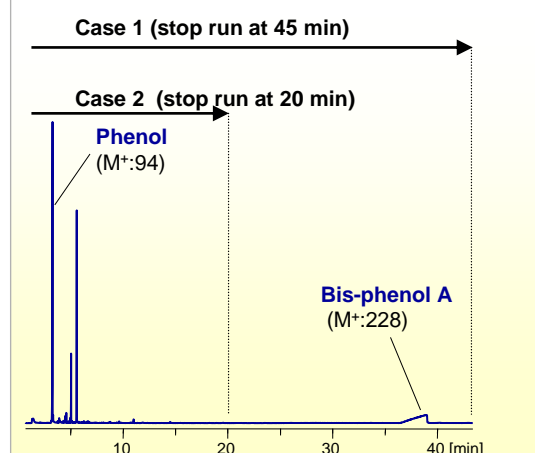dentified as "BT resin." Data 1 compares the search results from Case 1 and Case 2. The Case 1 chromatogram was acquired until 45 min; on the other hand, the Case 2 chromatogram was terminated after 20min. The BT resin is the first candidate in Case 1. BT resin-like structures are also nominated as possibilities 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 C40. 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.: 600ºC, Col: UA-5 (MS/HT) (30 m, 0.25 mm i.d., 0.25 µm)
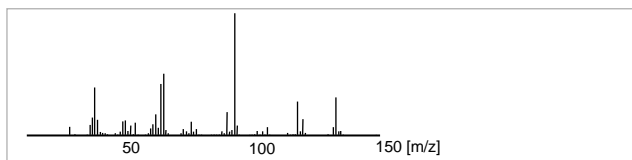
GC Oven: 60 - 170ºC (20ºC/min)

Case 1 (stop run at 45 min)

Case 2 (stop run at 20 min)

Phenol (M$^+$:94)

Bis-phenol A (M$^+$:228)

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

	Polymer/Additive	EntryID	Qual[%]
1	Bismaleimide triazine resin ; BT resin (C1-C40)	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
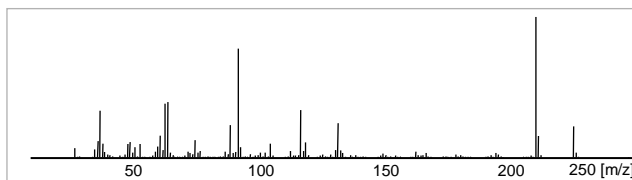
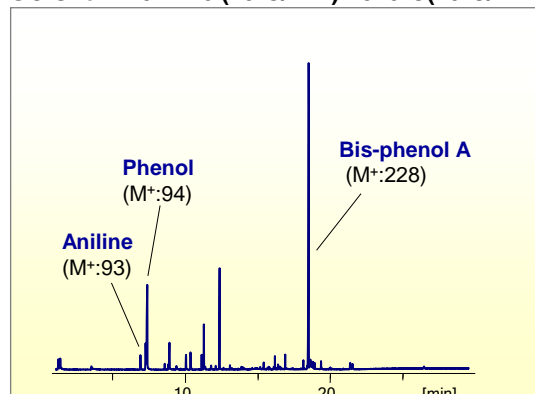**Case 2 (mass spectrum of the peaks detected from 0 to 20 min)**

	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	Bismaleimide triazine resin ; BT resin (C1-C20)	P(FL)-107	76

Data 2

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

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

Phenol (M$^+$:94)

Bis-phenol A (M$^+$:228)

Aniline (M$^+$:93)

Mass spectrum created from all the peaks detected

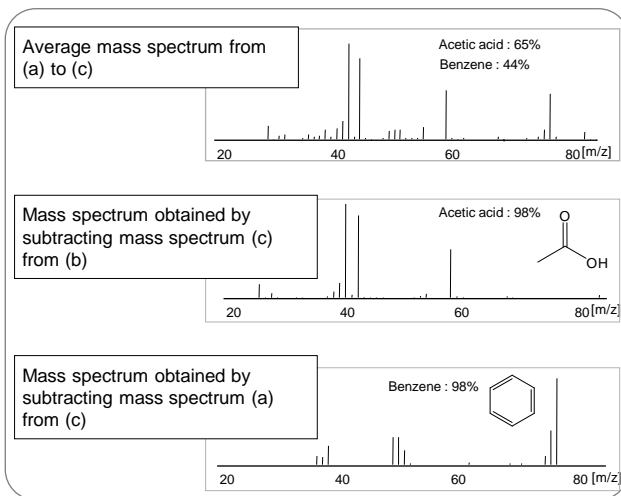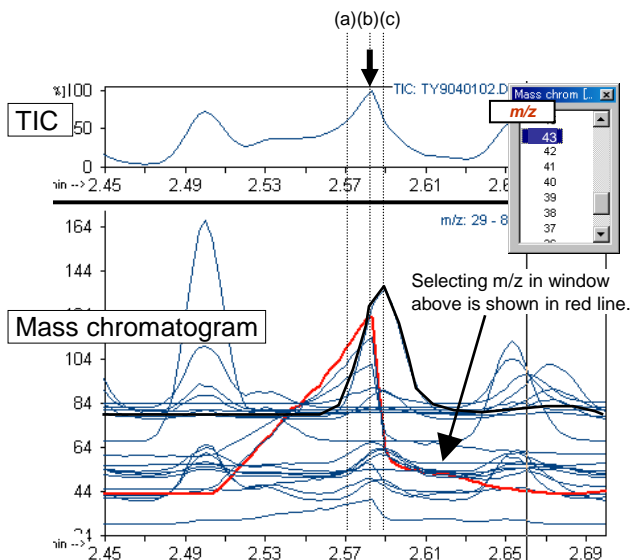|	Polymer/Additive	EntryID	Qual[%]
1	Bismaleimide triazine resin ; BT resin (C1-C40)	P(FL)-107	94
2	Polycarbonate (thermally stabilized) (C1-C40)	P(FL)-130	78
3	Polycarbonate (solvent method) ; SM-PC (C1-C40)	P(FL)-128	78
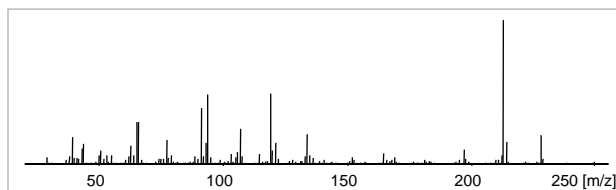
4. Two-dimensional multi-ion chromatograms allow you to obtain high quality mass spectra from overlapping peaks.

Pyrograms generally consists of complex pyrolyzates; therefore, it is very important to obtain high quality mass spectra of the targeted peak. F-search (Ver. 3.6) 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.

Selecting m/z in window above is shown in red line.

Average mass spectrum from (a) to (c)
Acetic acid : 65%
Benzene : 44%

Mass spectrum obtained by subtracting mass spectrum (c) from (b)
Acetic acid : 98%

Mass spectrum obtained by subtracting mass spectrum (a) from (c)
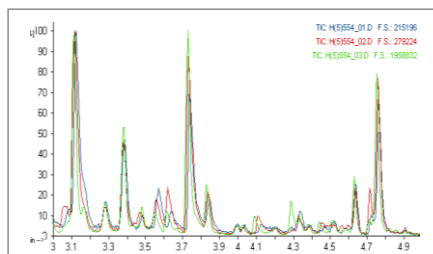Benzene : 98%

5. Overlay of multiple TICs

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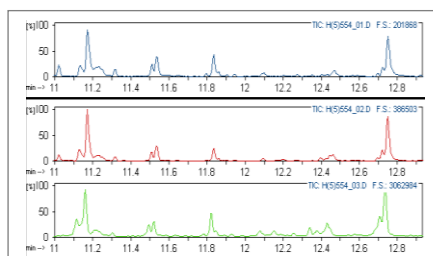
Separate display of TICs

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.

Background Subtraction
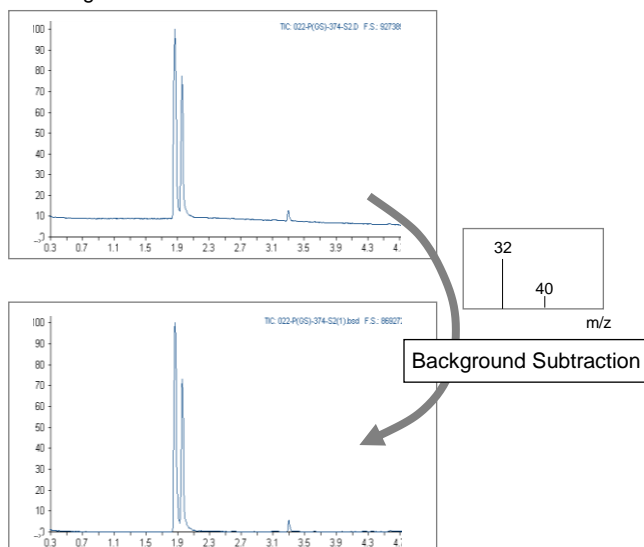
7. Now you can search NIST library directly from within F-Search (Ver. 3.6).

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. 3.6).

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

A: Evolved Gas Analysis
(with EGA-MS18B library)
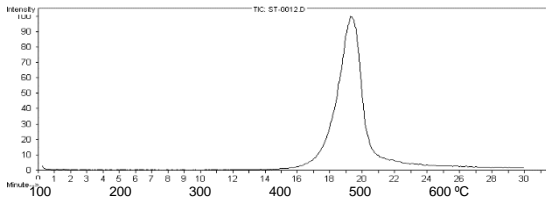This method allows simple thermal analysis of a sample. The thermogram provides the thermal property of the entire sample.
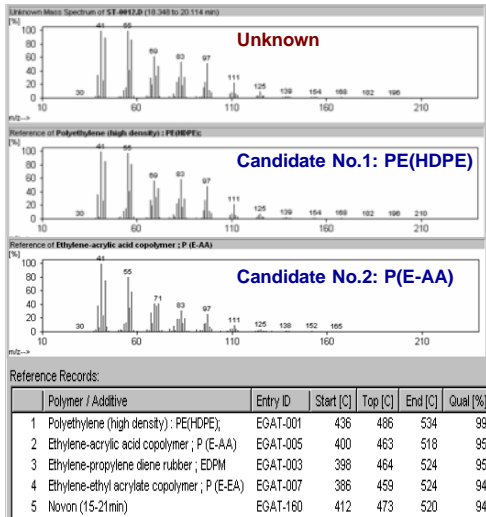
B: Py-GC Analysis
(with PyGC-MS18B library)
This technique offers detailed and advanced analysis of each peak on the pyrogram through analysis of mass spectra.

Obtain a thermogram using EGA-MS

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

Obtain a pyrogram using Py-GC/MS

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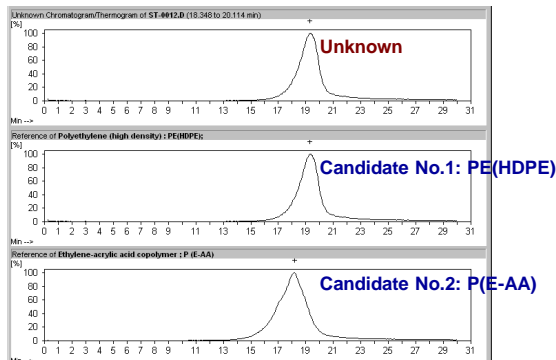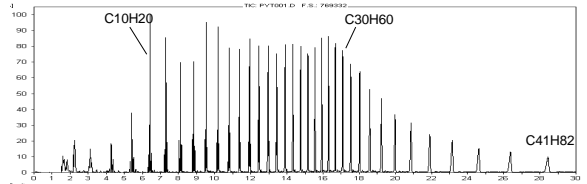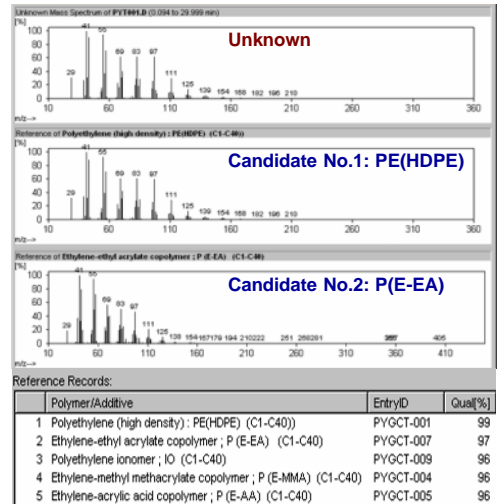GC Oven: 40(2 min) - 300ºC(20ºC/min)

The search results using the EGA-MS18B 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.

Reference Records:

|	Polymer / Additive	Entry ID	Start [C]	Top [C]	End [C]	Qual [%]
1	Polyethylene (high density) : PE(HDPE);	EGAT-001	436	486	534	99
2	Ethylene-acrylic acid copolymer ; P (E-AA)	EGAT-005	400	463	518	95
3	Ethylene-propylene diene rubber ; EDPM	EGAT-003	398	464	524	95
4	Ethylene-ethyl acrylate copolymer ; P (E-EA)	EGAT-007	386	459	524	94
5	Novon (15-21min)	EGAT-160	412	473	520	94

The search results using the PyGC-MS18B library

F-Search (Ver. 3.6) 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.

Reference Records:

	Polymer/Additive	EntryID	Qual[%]
1	Polyethylene (high density) : PE(HDPE) (C1-C40))	PYGCT-001	99
2	Ethylene-ethyl acrylate copolymer ; P (E-EA) (C1-C40)	PYGCT-007	97
3	Polyethylene ionomer ; IO (C1-C40)	PYGCT-009	96
4	Ethylene-methyl methacrylate copolymer ; P (E-MMA) (C1-C40)	PYGCT-004	96
5	Ethylene-acrylic acid copolymer ; P (E-AA) (C1-C40)	PYGCT-005	96

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. 2: P(E-AA) does not match with that of the unknown and can be eliminated from consideration.

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-EA) differs from that of the unknown sample and be eliminated from consideration.
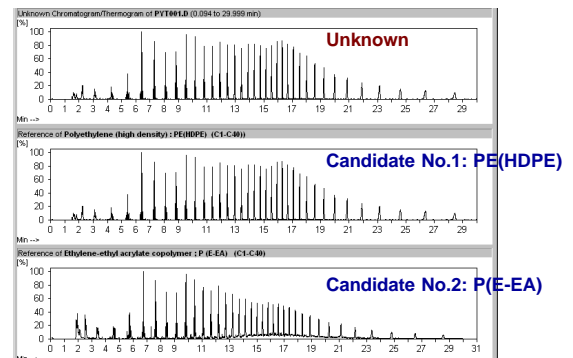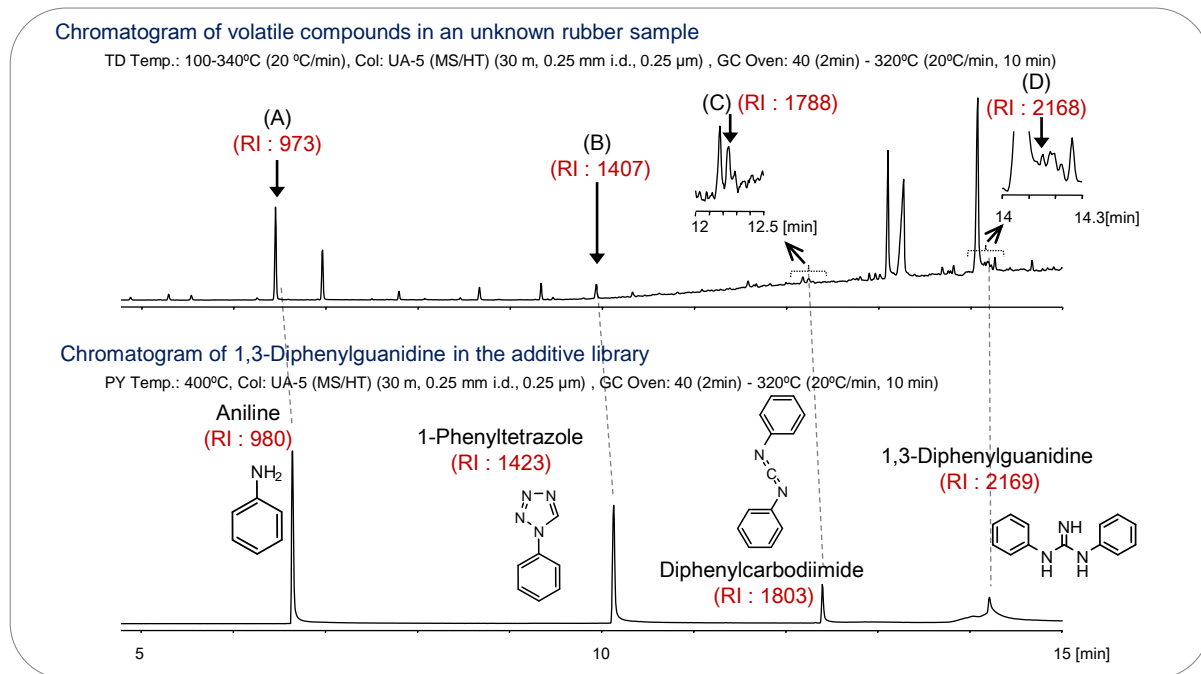

Conclusion : Based on the search results of both thermograms and pyrograms, the unknown sample was narrowed down from the candidate polymers to PE.

Analysis of vulcanization accelerator in rubber (ADD-MS16B library used)

The example below is the analysis of unknown vulcanization accelerator in a compounded rubber sample using TD-GC/MS technique. ADD-MS16B 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
TD Temp.: 100-340ºC (20 ºC/min), Col: UA-5 (MS/HT) (30 m, 0.25 mm i.d., 0.25 µm) , GC Oven: 40 (2min) - 320ºC (20ºC/min, 10 min)

(A) (RI : 973)
(B) (RI : 1407)
(C) (RI : 1788)
(D) (RI : 2168)

Chromatogram of 1,3-Diphenylguanidine in the additive library
PY Temp.: 400ºC, Col: UA-5 (MS/HT) (30 m, 0.25 mm i.d., 0.25 µm) , GC Oven: 40 (2min) - 320ºC (20ºC/min, 10 min)

Aniline (RI : 980)
1-Phenyltetrazole (RI : 1423)
Diphenylcarbodiimide (RI : 1803)
1,3-Diphenylguanidine (RI : 2169)

Search results of peak (D)

P...	Assignment	Polymer / Additive	Entry ID	Rt Idx	Rt Time	MW	Qual ...
1	1,3-Diphenylguanidine	1,3-Diphenylguanidine	V(1)-007	2169	14.21	211	97
2	Aniline	N,N'-Diphenylthiourea	V(1)-004	980	6.64	93	78
3	Aniline	1,3-Diphenylguanidine	V(1)-007	981	6.64	93	78
4	Aniline	n-Butylaldehyde-aniline reaction products	V(1)-003	980	6.65	93	77
5	Aniline	Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline	A(4)-110	980	6.76	93	76

Fig. 1 Library search of volatile compound from rubber sample using ADD-MS16B library

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

(Pyrolyzate-MS18B and PyGC-MS18B 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 (ver. 3.6) and Pyrolyzate-MS18B 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-MS18B 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.

Py Temp.: 400ºC, TMAH(25 wt%): 2 uL
Col: UA-5(MS/HT) (30 m, 0.25 mm i.d., 0.25 µm)
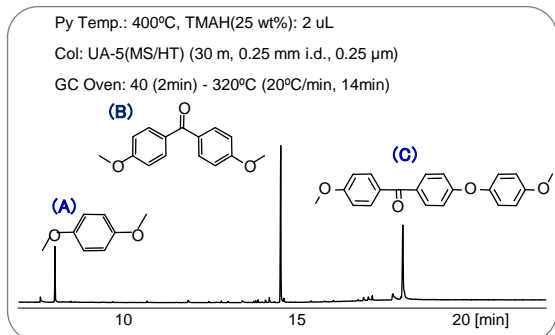GC Oven: 40 (2min) - 320ºC (20ºC/min, 14min)

(A) (B) (C)

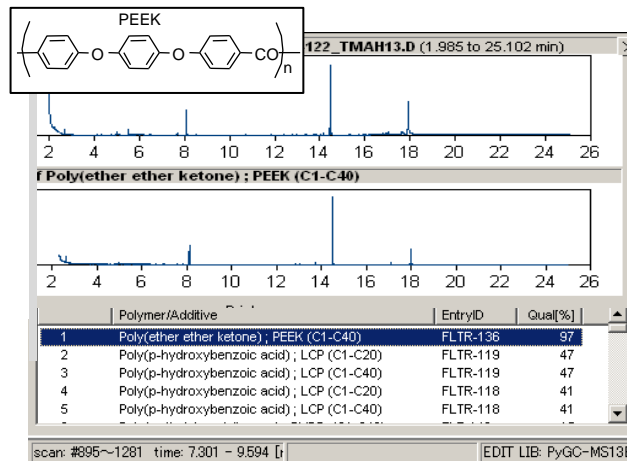Fig. 2 Library-search of methyl derivatives formed by THM using Pyrolyzate-MS18B library

Fig. 3 Polymer search results obtained using integration-summation mass spectrum and PyGC-MS18B library

Polymer search using pyrolyzates of pyrogram (Pyrolyzate-MS18B library used)

Using mass chromatograms, unknown polymers can be identified by searching the polymer library (PyGC-MS18B); 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

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 MS18B 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.

Pyrogram of unknown polymer

(A) and (B) below were identified by library search on NIST library; however, (C) and (E) could not be identified.
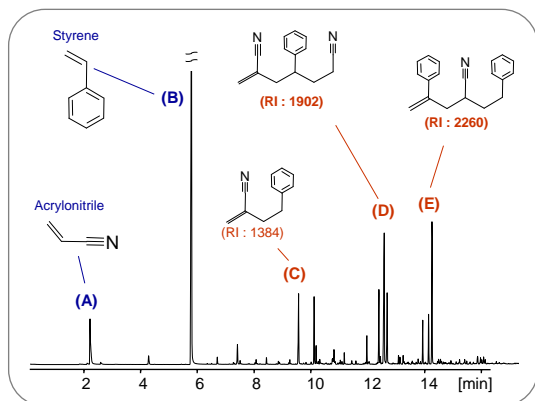
Py Temp.: 600ºC, Col: UA-5(MS/HT) 30 m, 0.25Φ, 0.25 µm
GC Oven: 40 (2 min) - 300ºC(20ºC/min)

Fig. D1 Pyrogram of unknown polymer

Search result for peak (E)

Pyrolyzate-MS18B 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.
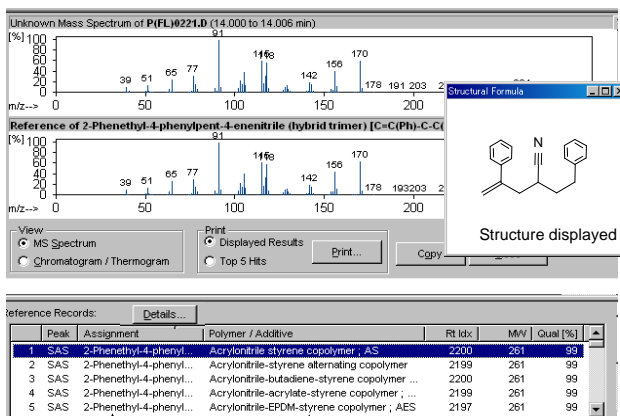
Pyrolyzate candidates generated upon library search.

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

Fig. 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. 3.6) 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.
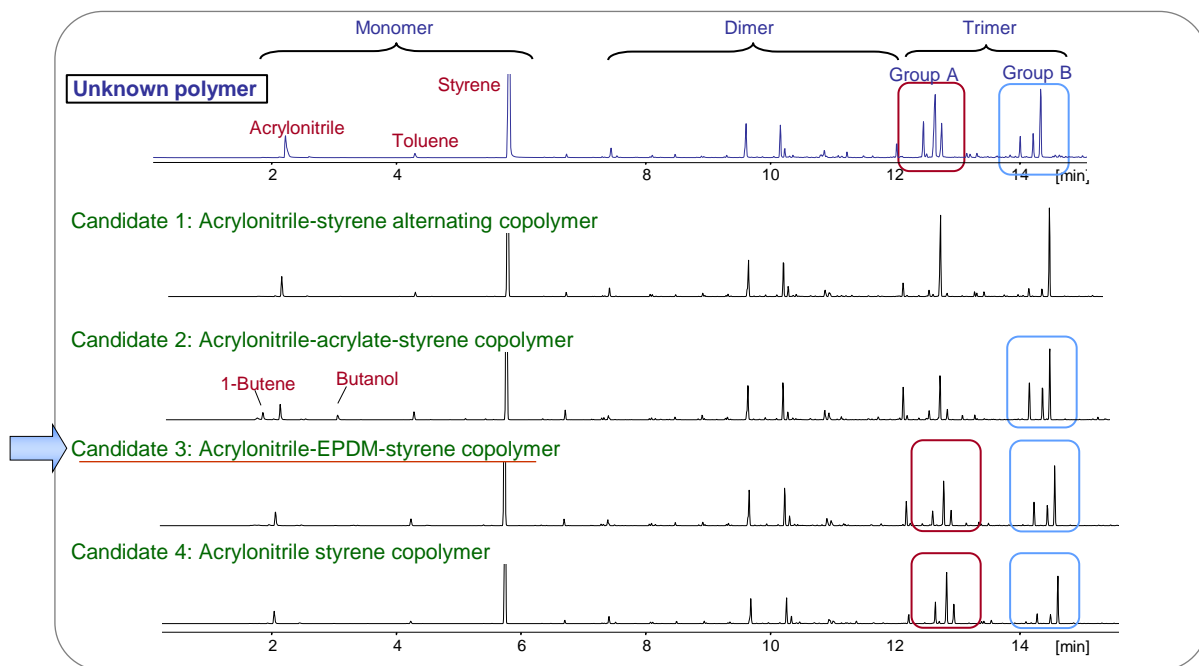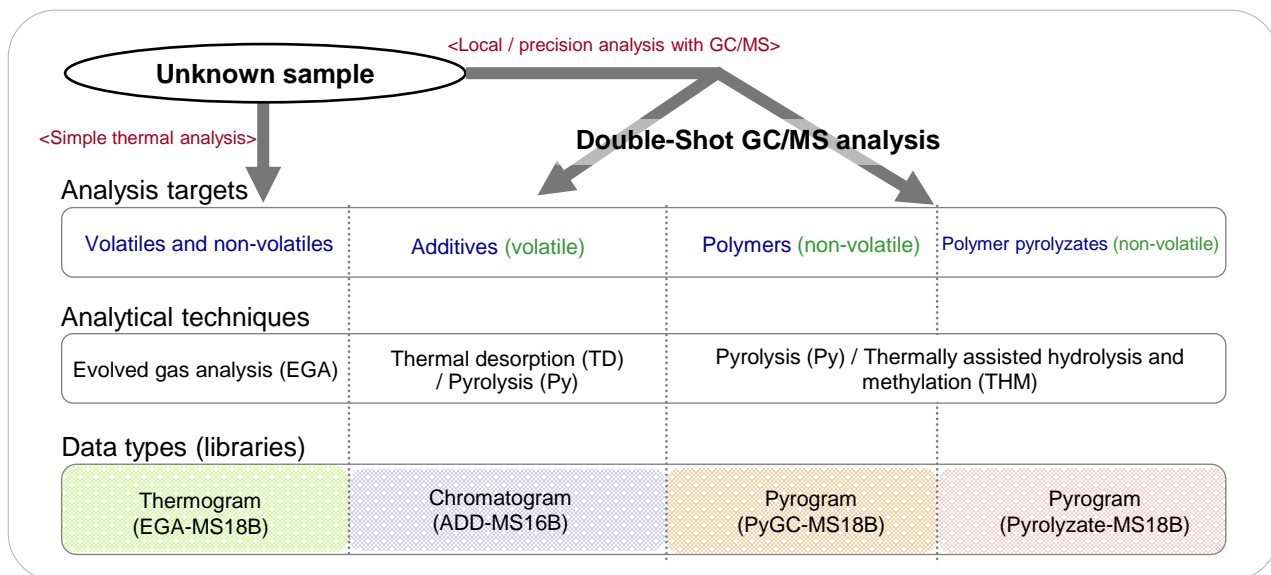

Fig. D3 Visual comparison of pyrograms of polymers stored in the library

<Local / precision analysis with GC/MS>

Unknown sample

<Simple thermal analysis>

Double-Shot GC/MS analysis

Analysis targets

Volatiles and non-volatiles	Additives (volatile)	Polymers (non-volatile)	Polymer pyrolyzates (non-volatile)

Analytical techniques

Evolved gas analysis (EGA)	Thermal desorption (TD) / Pyrolysis (Py)	Pyrolysis (Py) / Thermally assisted hydrolysis and methylation (THM)	

Data types (libraries)

Thermogram (EGA-MS18B)	Chromatogram (ADD-MS16B)	Pyrogram (PyGC-MS18B)	Pyrogram (Pyrolyzate-MS18B)

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

Product name (P/N)	F-Search "All-In-One" (PY-1110E-181)	Optional libraries (search software F-Search (Ver. 3.6) (PY-1111E-181) required)			
		EGA-MS18B (PY-1112E-181)	PyGC-MS18B (PY-1113E-181)	Pyrolyzate-MS18B (PY-1115E-181)	ADD-MS16B (PY-1114E-161)
Analytical technique	Package contains F-Search (Ver. 3.6) 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		1,000 polymers	1,000 polymers (THM data in 33 polymers)	268 polymers (THM data in 33 polymers)	494 additives (Py and TD data in 110 additives)
Stored chromatogram		Thermogram	Pyrogram/chromatogram		
Number of mass spectra		c.a. 1,900	c.a. 2,800	c.a. 5,500	c.a. 4,800
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		Compatible with all major GC/MS systems. (Data formats used in Agilent(MassHunter, Chemstation), Shimadzu, and JOEL(AutoMass, GCMate, K9, Q1500) can directly be read. Thermo, Varian, PerkinElmer, LECO require conversion to AIA format.)			
PC system required		OS : Windows 10, 8.1 (64 bit or 32 bit) minimum hard disk space 250MB			

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

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