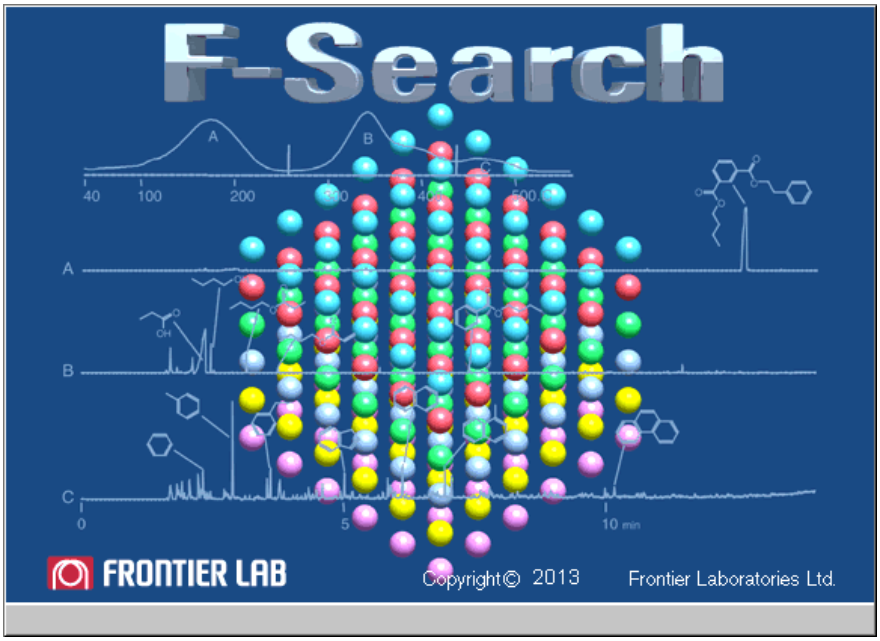
F-Search System

“All-in-One” (PY-1110E-161)

(Mass Spectral Libraries for Polymers and Additives, and Search software)

OPERATIONS MANUAL



FRONTIER LABORATORIES LTD.

CHECKING CONTENTS IN PACKAGE

The F-Search All-in-One (PY-1110E-161) includes products listed below. Check to see everything is included in the package. If anything is missing, please contact your sales representatives or Frontier Laboratories directly.

	Product	Product number	Quantity
Search software	F-Search (Ver. 3.5)	(PY-1111E-161)	1
Libraries	EGA-MS14B library	(PY-1112E-141)	1
	PyGC-MS14B library	(PY-1113E-141)	1
	ADD-MS16B library	(PY-1114E-161)	1
	Pyrolyzate-MS13B library	(PY-1115E-131)	1
	Manual (this manual)		1

Note: A password issued by Frontier Laboratories is required to use this software. Two passwords will be issued for each CD-ROM. See Chapter 3 for details.

Frontier Laboratories Ltd. will not be liable for results and information obtained using this software product.

This manual contains descriptions for F-Search, EGA-MS14B library, PyGC-MS14B library, ADD-MS16B library and Pyrolyzate-MS13B library.

About quality of Additive Py-GC/MS library

Thank you for purchasing Additive Py-GC/MS library (ADD-MS16B library: PY-1114E-161). Read this manual thoroughly in order to take full advantages of this library.

Mass spectra stored in this library contains spectra of a variety of chromatographic peaks of pyrolyzates obtained by pyrolysis of addtives at 600ºC using a micro furnace pyrolyzer. At high temperature of 600ºC, some additives decompose and some do not; therefore, a number of peaks ranging from small to large peaks are observed. Generally, the quality of a mass spectrum depends on the chromatographic peak intensity. Normally, mass spectra from small peaks suffer from a lot of noise, and often without parent peaks. These spectra are, in general, not used for identification of unknowns. However, such mass spectra may be of value for unknown identification when utilizing the retention indecies together. Therefore, this library contains mass spectra obtained from such small chromatographic peaks.

CHAPTER 1 INTRODUCTION

Thank you for purchasing Frontier Laboratories' polymer/additives libraries and the F-Search software. The F-Search software allows you to easily compare data from unknown polymers and their additives with data obtained via Evolved Gas Analysis (EGA)-MS and Pyrolysis (Py)-GC/MS.

Although a large amount of information can easily be extracted from the EGA and Py-GC analysis of a sample, the characterization is often difficult. Many times researchers and quality assurance personnel must depend on their intuition and experience to identify an "unknown". In order to provide a more objective means of identification. Frontier Laboratories developed the Multi-Shot Pyrolyzer which utilizes a temperature programmable furnace. The pyrolyzer can be used for evolved gas analysis (EGA); a technique which provides a thermal profile of all the constituents of a sample.

In the "ADD-MS16B library" which contains 494 polymer additives,110 of which includes thermal desorption data obtained at 400ºC together with mass spectra of additives and retention indices, in addition to pyrolyzate data of additives.

We recommend that you read this manual thoroughly before attempting to use this product.

Japanese patent : 3801355
US patent : 6444979 B1

CHAPTER 2 LIBRARIES SPECIFICATIONS

• Polymers : 700 polymers in EGA-MS library

700 polymers in PyGC-MS library (THM-GC/MS data stored for 33 polymers)

165 polymers in Pyrolyzate-MS library (THM-GC/MS data stored for 33 polymers)

All the polymers included 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. are included.

• Additives : ADD-MS library contains 494 additives (thermal desorption data obtained at 400ºC for 110 additives are stored) including the major organic additives found in "Standard Spectra and Data Compilation of Polymer Additives '94/95", S. Tsuge, M. Takayama, 1994, Japan Scientific Information KK.

• Data set includes the compound name, molecular formula, molecular weight, analytical conditions and the spectral range.

• Data format : Bar type data (commonly used in quadrupole GC/MS)

• Spectra stored

EGA-MS14B library	: 1381
PyGC-MS14B library	: 2014
ADD-MS16B library	: 4819
Pyrolyzate-MS13B library	: 3173

• Chromatograms stored

EGA-MS14B library	: 700
PyGC-MS14B library	: 733
ADD-MS16B library	: 603
Pyrolyzate-MS13B library	: 198

• Media : 1 CD-ROM

• PC Requirements

: Microsoft Windows 10, 8.1, 8, 7, Vista, XP (64 bit or 32 bit, respectively)

• Required hard disk space : 200MB

• Mass spectral data formats : Agilent (ChemStation), JEOL, Shimadzu

Other mass spectral data format : NetCDF (AIA format)

CHAPTER 3 INSTALLING F-Search (Search software)

3.1 Customers who have older versions of the F-Search software

3.1.1 Notes on installing F-Search

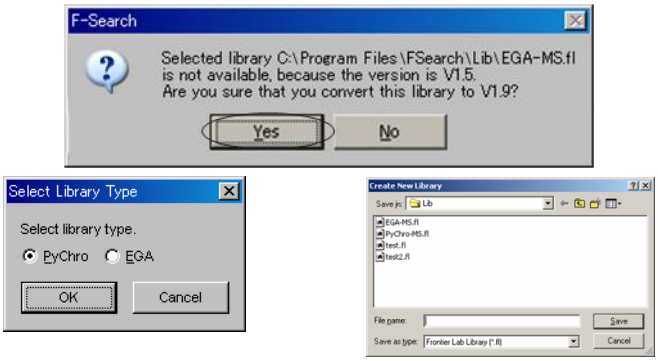
To install the update for F-Search ver. 3.5 (PY-1110E-U16x, or PY-1111E-U16x): Do not uninstall older versions of F-Search. Simply start the installation and follow the instructions.

> User libraries (file extension: ".fl") created by customer will not be deleted; however, we recommend that you have copies at different location.

3.1.2 Notes on using libraries earlier than version 1.13

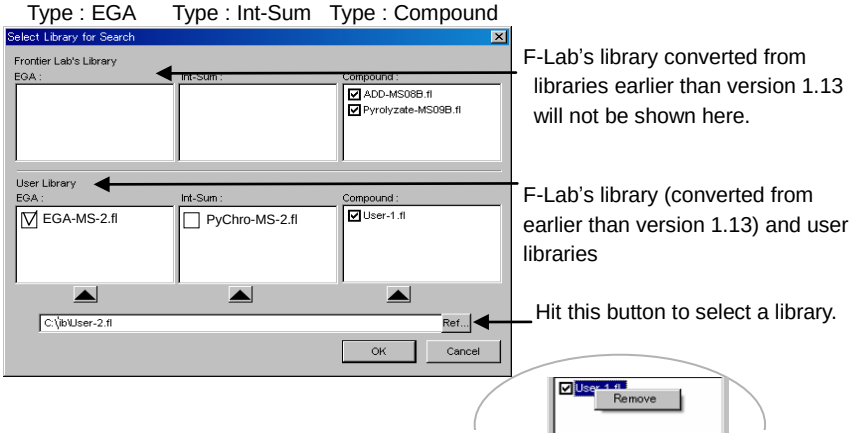
Libraries used with F-Search ver. 1.13 or earlier and user libraries created by version 1.13 or earlier need to be converted before using them with this version of F-Search. The conversion procedure is shown in Fig 3.1. When starting F-Search or loading a library created using an older version, you will be "asked" if you would like to convert it: Click [Yes] to convert it to a new library format (see section 5.1.12 in the operations manual for the procedure). Then select either PyChro library or EGA library, enter a new library file name. Note that you cannot overwrite an existing library file.

Libraries used with older versions do not contain certain data such as the time range in which a mass spectrum was created and the temperature range over which EGA data was collected. F-Search will automatically assign default values for them. The converted libraries are not automatically loaded like Frontier Laboratories libraries. Settings similar to selecting user libraries as shown in section 5.1.12 in the operations manual are required before converted libraries become searchable.



(a) Converting process

From the menu bar, select [Library] - [Select Library for Search]



To remove a library from this list, click the right mouse button and select "Remove". (Note that the actual user library stays intact.)

(b) Select library for search

Fig. 3-1 Converting a ver 1.13 or older versions of library to the latest version

3.1.2 Notes on using Ver. 2.0x libraries

Versions 2.0x Frontier Laboratories libraries need data conversion before they can be searched by the latest version of F-Search. The procedure is shown in Fig. 3.2. When F-Search starts or an old version of library is loaded, you will be asked if you would like to convert it, select [Yes] to convert it[*1] (see section 5.1.12 in the operations manual for the procedure). Next, select a library type from among EGA, PyGC and Additive[*2]. If the converted libraries are located in the "Lib" folder immediately below the folder where F-Search has been installed (default location is C:\ Program Files\FSearch\), the libraries are automatically loaded

when F-Search starts up.

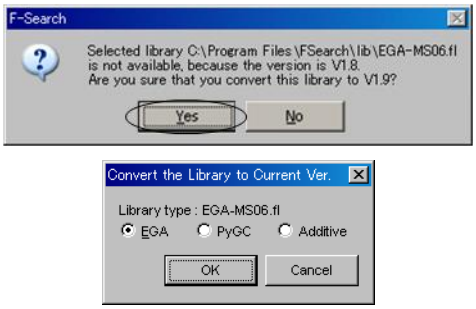


Fig. 3-2 Converting libraries from version 2.0x to the current version

*1 If [No] is selected, you will be “asked” if you would like to convert the libraries every time F-Search starts up. To avoid this, move the old libraries located in “Lib” folder immediately below the folder where F-Search has been installed (default folder is C:\Program Files\FSearch\) to a new location.

*2 If the wrong library type has been selected, from the F-Search menu bar, select [Library] - [Select Libraries for search…] to display a window shown in Fig. 3.3, then right-click on a library to convert it to the correct library type.

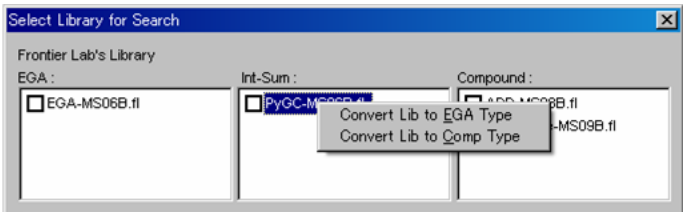


Fig. 3-3 Resetting library type

3.2 Installing software

3.2.1 Installing F-Search search software (PY-1110E-161, PY-1111E-161)

Insert the F-Search CD-ROM into the CD-ROM drive. The installer program will automatically start. Follow the instructions to complete the installation.

(1) Select [Start] - [Program] - [F-Search]. A dialog box shown in Fig. 3-4 will be displayed. Enter the password to open the program (Fig. 3-4B).

(2) The password is obtained on our website (http://www.frontier-lab.com/).

(3) Please complete the user registration when obtaining a password. You must know the PcID (shown in A of Fig. 3-4) and the serial number of the F-Search software (printed on the CD-ROM) prior to opening our website, select [Support] - [Password] – [F-Search Password] to find [User registration/Create password] page. Follow the instructions displayed on the screen. The password will be issued and displayed on the screen. Also, it will automatically be sent to the registered e-mail address.

(4) If you do not have access to our website, send the PcID and the serial number of the F-Search software (printed on the CD-ROM) to Frontier Laboratories either by email (cs@frontier-lab.com) or by FAX (+81-24-935-5102). Please include your contact name and address. In urgent cases, you can call our customer support department at +81-24-935-5100.

(5) Enter the password into B of Fig. 3-4 and click [OK]. This will remove the protection and the window shown in Fig. 3.5 will be displayed.

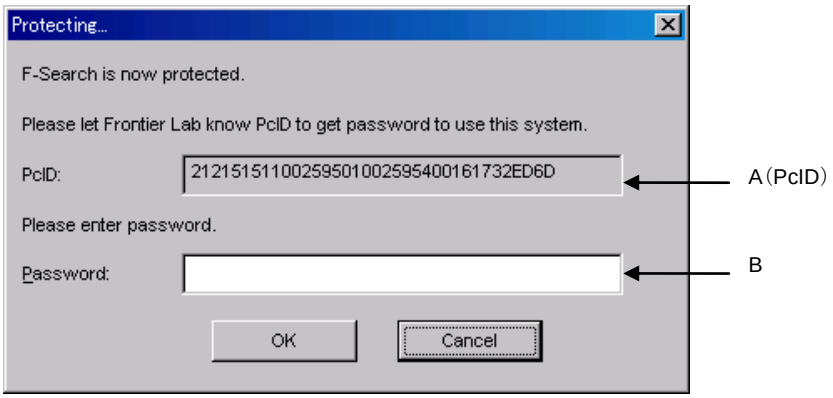


Fig. 3-4 Dialog box for entering password to remove software security

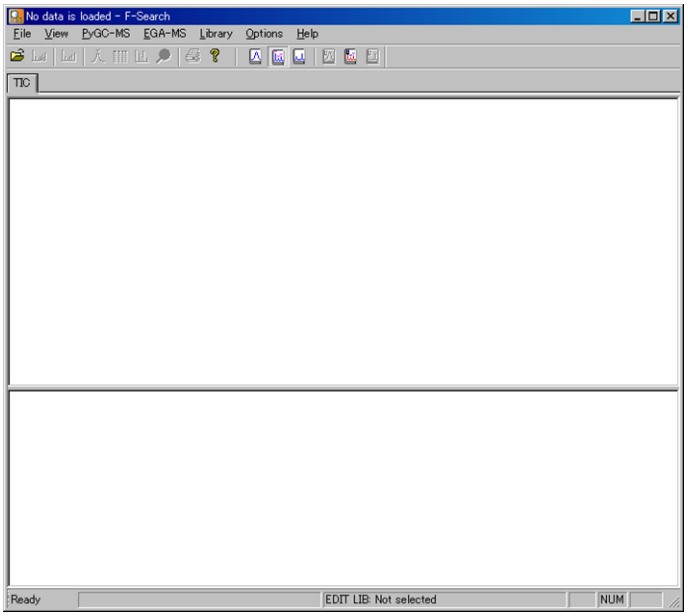


Fig. 3-5 F-Search startup screen after removing the software security

3.2.2 Uninstalling F-Search (PY-1110E-161, PY-1111E-161)

The search program and libraries can be removed from the hard drive of your PC. To uninstall, select [Start] - [Program] - [F-Search] - [Uninstall]. Alternatively, the program can be uninstalled by selecting [Start] - [Control Panel] - [Add/Remove Programs] - [F-Search].

3.2.3 Installing libraries (PY-1112E-141, PY-1113E-141, PY-1114E-161 and PY-1115E-131)

Insert the CD-ROM into the drive. The installer will start up. Follow the instructions to complete the installation. Note that the libraries must be installed into the same folder as the main program. Library files will be placed in the "Lib" folder, located immediately below the program folder.

3.2.4 Uninstalling libraries (PY-1112E-141, PY-1113E-141, PY-1114E-161 and PY-1115-131E)

There is no uninstaller program available to remove the libraries. To delete the libraries, go to the "Windows Explorer" and delete the files.

CHAPTER 4 OVERVIEW of LIBRARIES

4.1 Evolved Gas Analysis (EGA) and Pyrolysis Gas Chromatography (Py-GC)

4.1.1 Evolved Gas Analysis

International Confederation for Thermal Analysis (ICTA) defines Evolved Gas Analysis as "A technique to determine types and/or quantities of volatile components evolved from a material as a function of temperature by varying the material temperature according to a controlled program."

4.1.2 Pyrolysis Gas Chromatography

Pyrolysis Gas Chromatography (Py-GC) is a technique in which a sample is degraded at a constant temperature (generally between 400 and 800ºC in an inert carrier gas such as Helium). The pyrolyzer is directly connected to the injection port of a GC, and the pyrolyzates are separated on a GC separation column. A plot of response v. elution time (RT) is referred to as a “pyrogram”.

4.2 About the polymers and additives found in the libraries

4.2.1 Polymers

The libraries contain data of 700 polymers. All of these polymers are typical polymers commercially available. Several newly developed or specially modified polymers are also included. For a complete list of the polymers, see Polymer-MS_List.pdf (the default location is C:\Program files\Fsearch\List\).

4.2.2 Additives

358 additives are stored in the library. These are typical additives which are widely used in the industry. For a complete list of additives, see Add-MS_List.pdf (the default location is C:\Program files\Fsearch\List\).

4.3 Contents of the F-Search libraries

4.3.1 Data stored in both Polymer & Additive libraries

Stored in both the polymer and additive libraries are the temperature programs for the pyrolyzer furnace, the GC oven, and the GC separation column. Also listed are the carrier gas, and the MS data acquisition settings.

4.3.2 EGA-MS library

The EGA-MS library is a collection of background-subtracted mass spectra obtained from the main peaks in the polymer EGA thermogram. As shown in Fig. 4-1, the polymer name, chemical formula, retention time range, programmed temperature parameters, etc are stored in this library.

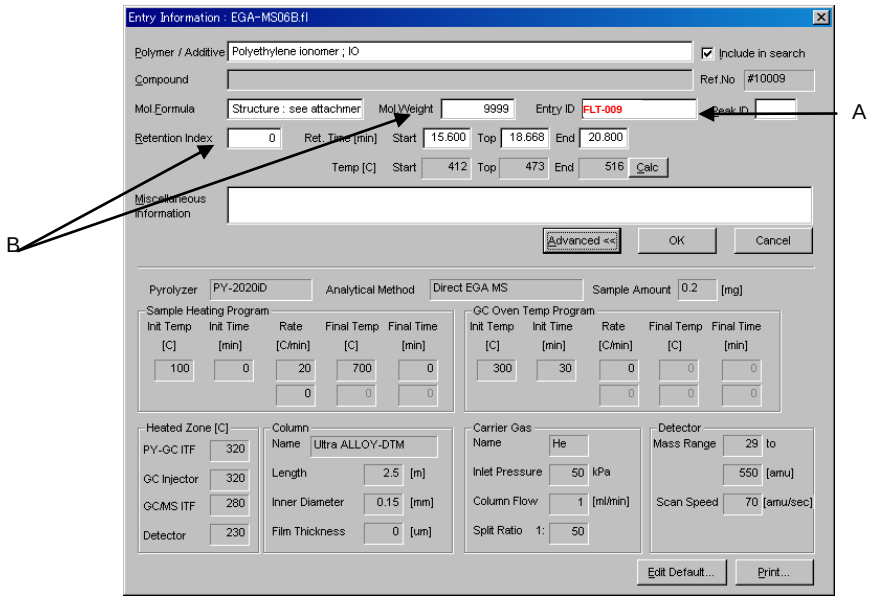


Fig. 4-1 A typical record in the EGA-MS library

A : Number with FLT shown in Entry ID is a unique polymer number assigned to each pyrograms as listed in "Pyrolysis-GC/MS of High polymers -- Fundamentals and Pyrogram Compilations" by S. Tsuge, H. Ohtani and C. Watanabe. This is very useful for checking pyrograms obtained by Py-GC and making a qualitative assessment of the data.

B : Entries for the Mol.Weight - 9999 and Retention Index - 0 means that these values are unavailable.

4.3.3 PyGC-MS library

The PyGC-MS14B library is a collection of mass spectra. First, all the total ion peaks are integrated (INT.). Then, the spectra are grouped: C1 through C10, C1 through C20, and C1 through C40. The mass spectra in each group are added together (SUM.). As shown in Fig. 4-2, the polymer name, molecular formula, peak detection time range, etc are stored as a record in the PyGC-MS library.

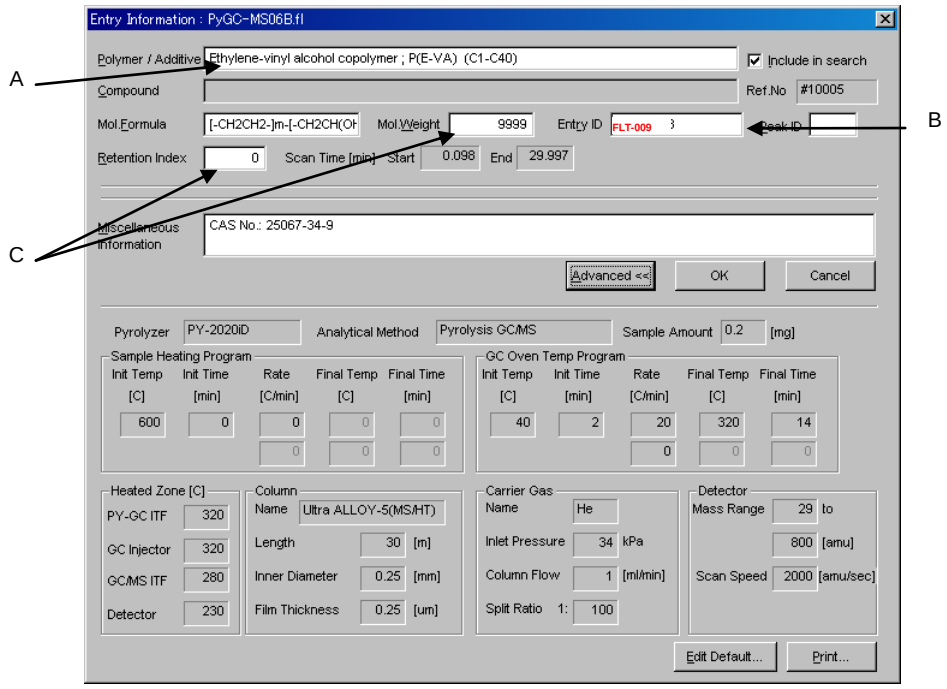


Fig. 4-2 A typical record in the PyGC-MS14B library

A : Indicates that this is an INT-SUM spectrum of polystyrene with a data acquisition range from C1 through C40.

B : Number with FLT shown in Entry ID is a unique polymer number assigned to each pyrograms as listed in "Pyrolysis-GC/MS of High polymers --Fundamentals and Pyrogram Compilations" by S. Tsuge, H. Ohtani and C. Watanabe. This is very useful for checking pyrograms obtained by Py-GC and making a qualitative assessment of the data.

C : Entries for the Mol.Weight – 9999 and Retention Index - 0 mean that these values are unavailable

4.3.4 ADD-MS library

The ADD-MS library consists of many records each of which contains the average mass spectrum of each peak in the pyrogram and the average mass spectrum of unresolved peaks, if present. As shown in Fig. 4-3, the chemical name, composition formula, peak top retention time, retention index, and name of the additive used to obtain the data are shown.

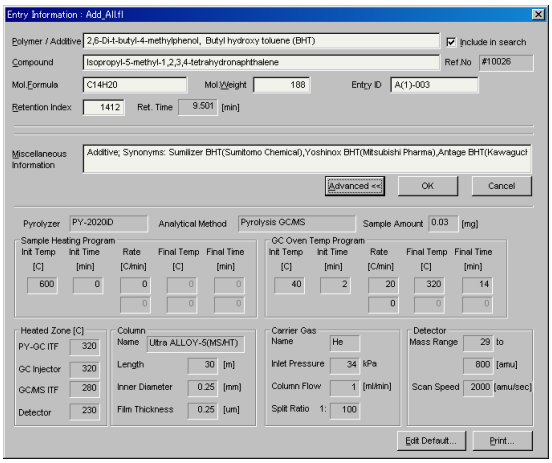


Fig. 4-3 A typical record in ADD-MS library

4.3.5 Pyrolyzate-MS library

The Pyrolyzate-MS13B library consists of the average mass spectrum of each peak in the pyrogram. As shown in Fig. 4.4, a record contains the chemical name, the composition formula, peak-top retention time, retention index, and the name of the polymer used to generate the data.

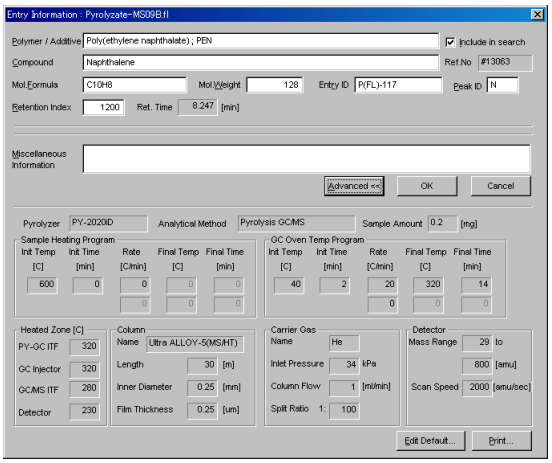


Fig. 4-4 A record stored in Pyrolyzate-MS13B library

4.4 Difference in mass spectra obtained between EGA-MS and Py-GC/MS

The Evolved Gas Analysis (EGA) thermogram provides information on the thermal properties of the sample. The combined mass spectra over time also contains information which can be used to help characterize the sample. With flash pyrolysis (Py-GC) the

sample is degraded within tens of a millisecond. The degradation products or pyrolyzates, provide information on the original polymer structure. The difference between the two techniques involves the rate of heating; each provides thermal data about the sample that, when combined, enables the analyst to fully characterize the sample.
The heating rate for EGA is normally 20ºC/min, while the rate for Py-GC is on the order of 600ºC/20msec (or 1,800,000ºC/min). When using EGA, secondary reactions must be taken into consideration, whereas only the primary reactions need to be considered in Py-GC.

Let us take a look at the differences between EGA and Py-GC in terms of compound fragmentation. There is little difference between the EGA and Py-GC spectra when analyzing depolymerizable polymers, such as polymethyl methacrylate (PMA) and polytetrafluoroethylene (PTFE).

However, polymers such as polyvinyl chloride (PVC), polyvinyl acetate (PVAc), and polyvinyl alcohol (PVA) which have polar groups on the side chain of the polymer backbone behave much differently. These polymers undergo elimination reactions between the side chain and neighboring hydrogen atoms so that a large amount of hydrogen chloride, acetic acid, or water at lower temperatures than those for main chain scissions are released. The main chain forms double bonds to give polyene structures. In EGA analysis, after the elimination reactions occur, further heating produces aromatic compounds via the aromatization of the fragments produced by the thermal decomposition of the polymer backbone; or via secondary reactions, various complex products are generated. In Py-GC, however, because pyrolysis occurs in an extremely short periods of time (tens of milliseconds), the secondary reactions are of no importance and the pyrolyzate fragments are, therefore, much simpler than those found in EGA data.

As shown in Fig. 4-5 (A), the EGA thermogram of PVC contains two broad peaks that are due to the elimination of hydrogen chloride at low temperature, and thermal decomposition of the main polymeric chain in high temperature. On the other hand, the pyrogram obtained by PyGC shown in Fig. 4-5 (B) provides information on the polymer structure. As shown above, these two data sets are complementary and when combined facilitate the qualitative analysis of the PVC sample. This is an example where spectra stored in the EGA-MS and PyGC-MS libraries are almost identical.

In the EGA-MS library, when two peaks are obtained from a single sample as observed in the example above, three spectra are stored in the library: (a) and (b) the average mass spectrum for each of two peaks and (c) the mass spectrum for the entire profile. In the

PyGC-MS library, the mass spectrum for each of the GC peaks (automatically detected) are integrated, and such spectra are summed over the three ranges (C1~C10, C1~C20, and C1~C40). The resultant spectrum is the basic data stored in the library. Therefore, library search results for an unknown polymer are most meaningful when results from both libraries are combined.

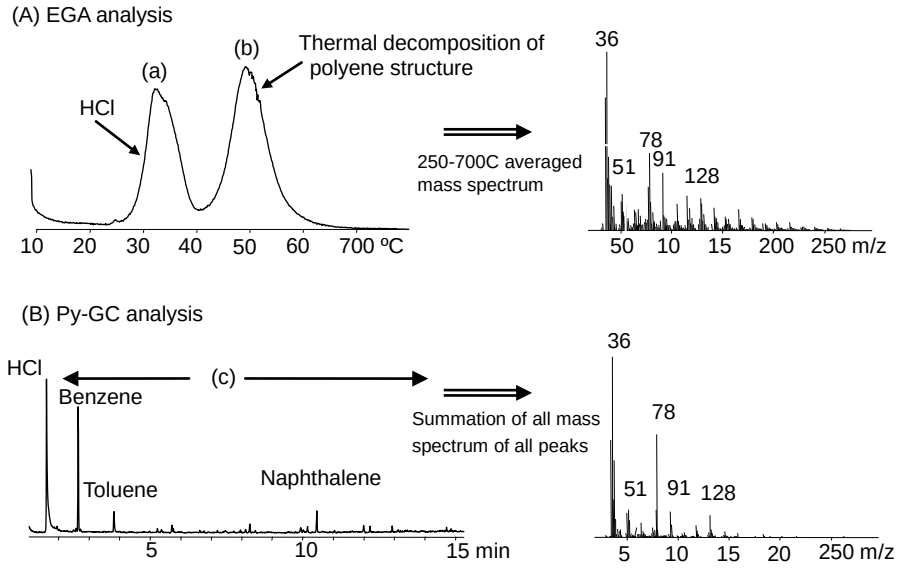


Fig. 4-5 Results of the analysis of PVC by EGA and Py-GC

CHAPTER 5 USING F-Search (Search software)

5.1 Basic operations of F-Search

5.1.1 Loading mass data file

(1) First, the manufacturer of your mass spectrometer must be specified. As shown in Fig. 5-1, select [Options] - [MS Data Type], and choose one of manufacturers among [Agilent], [JEOL], [Shimadzu] and [NetCDF].

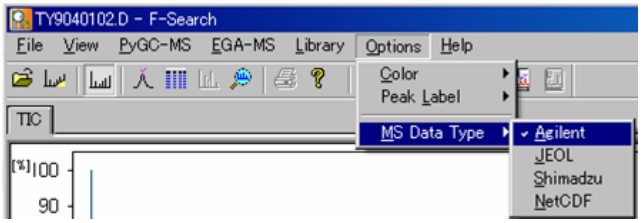


Fig. 5-1 Specifying data type

(2) As shown in Fig. 5-2, select [File] - [Load]. Then choose an MS data file in the window displayed, and press [OK] button. A chromatogram/thermogram will be displayed.

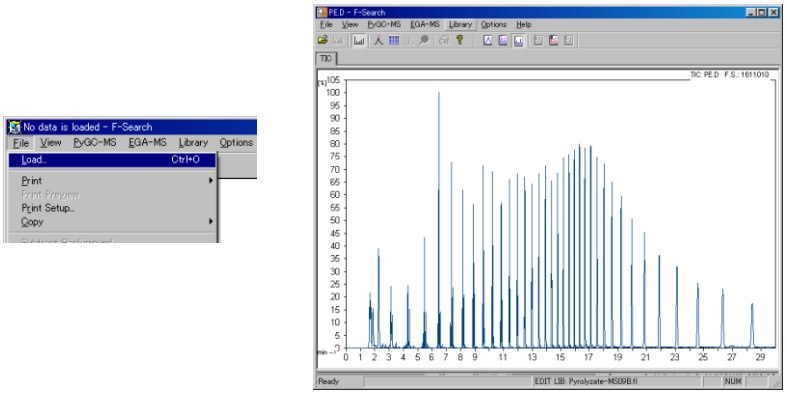


Fig. 5-2 Loading an MS data file and displaying a chromatogram

5.1.2 Expanding a chromatogram

In the chromatogram window, hold down the left-mouse button and drag the mouse pointer to select the area you desire to expand. Upon releasing the left-mouse button, the desired area of the chromatogram is displayed in the expanded view. To return to the normal display, double click the left mouse button anywhere on the chromatogram window.

5.1.3 Displaying a mass spectrum

In the chromatogram window, move the cursor to the time you desire to view the mass spectrum and double click the right-mouse button. The mass spectrum is displayed in the mass spectrum window. Follow the procedure outlined in section 5.1.2 to expand a desired portion of the mass spectrum.

5.1.4 Creating an averaged mass spectrum

To create an averaged mass spectrum over any time interval, hold down the right-mouse button and drag the mouse pointer from the start time to the end time in the chromatogram window.

5.1.5 Subtracting a background spectrum

Background spectrum can be subtracted from a mass spectrum. In the same manner as mentioned in section 5.1.3 or 5.1.4, first create a mass spectrum (A) and display it on the screen. Next, create a background mass spectrum (B). Then go to the menu and select [PyGC-MS] - [Subtract] to obtain a (A) - (B) spectrum, or alternatively, select [EGA-MS] - [Subtract] to generate the same result.

5.1.6 Displaying a mass table

As shown in Fig. 5-3, a mass table listing of m/z and intensity can be displayed by selecting [View] - [Mass Table...].

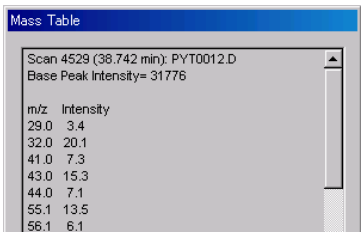
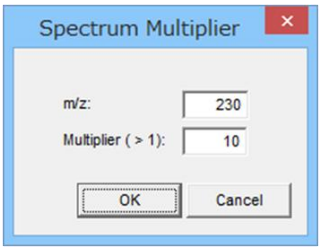


Fig. 5-3 Viewing a mass table

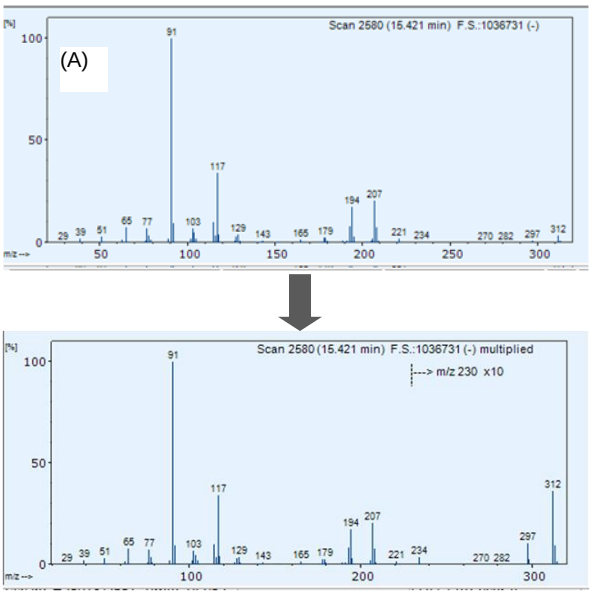
5.1.7 Viewing a specified range of a mass spectrum in expanded mode

A specified range of a mass spectrum such as molecular ion region can be viewed in expanded mode. As described in section 5.1.3 or 5.1.4, first create a mass spectrum (A) and display it. Now, from the menu bar, select [View] – [Spectrum Multiply…]. A dialog box shown in Fig. 5-4(a) is displayed. Enter a lower limit of m/z and magnification. As shown in

Fig. 5-4(b), specified range of the mass spectrum will be displayed in expanded mode.



(a) m/z range and multiplier



(b) Mass spectrum in expand mode

Fig. 5-4 Mass spectrum in expand mode

5.1.8 Printing a chromatogram and a mass spectrum

To print a chromatogram, a mass spectrum, or both, go to the menu bar and select [File] - [Print].

5.1.9 Copying a chromatogram and a mass spectrum to the clipboard

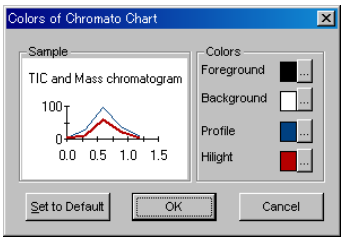
To copy a chromatogram or a mass spectrum to the clipboard, go to the menu bar and select [File] - [Copy]. The copied spectrum can be pasted into a Power Point file. “Ungroup” the spectrum before changing fonts and line thickness.

5.1.10 Setting the colors of the chromatogram and a mass spectrum and turning on peak labels

By selecting [Options] - [Color] from the menu bar, the color attributes of a spectrum chart can be changed as shown in Fig. 5-5. Clicking on the [Default] button automatically sets colors to the default color scheme.

As shown in Fig. 5-22, (1) the retention time can be added at the top of each peak in the

chromatogram and (2) the mass number can be added at the top of the main peak in a mass spectrum. From the menu [Options] - [Peak Label], turn ON or OFF labeling. The distance from the peak top to the label can be adjusted by entering a number in pixel.



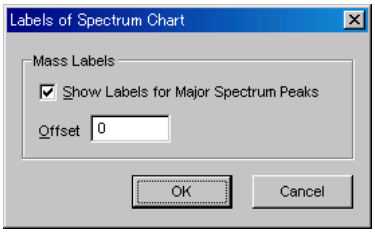
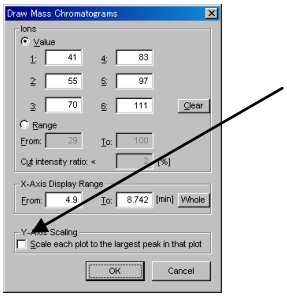


Fig. 5-5 Setting colors of chart

Fig. 5-6 Turning on/off labeling of chart

5.1.11 Viewing a mass chromatogram

A mass chromatogram (extracted ion chromatogram) is a plot of a specific ion (m/z) abundance plotted against time. From the menu bar, select [View] - [Mass Chromatograms]. The dialog box shown in Fig. 5-7 will be displayed. A maximum of six mass numbers (m/z) can be entered. Double clicking the right-mouse button anywhere on a mass chromatogram will produce a spectrum at the bottom most row. It can be displayed after the background spectrum is subtracted. To view the TIC and mass spectra, select [View] - [TIC].



Check here to normalize the largest peak to 100.

Fig. 5-7 Setting parameters to view mass chromatograms

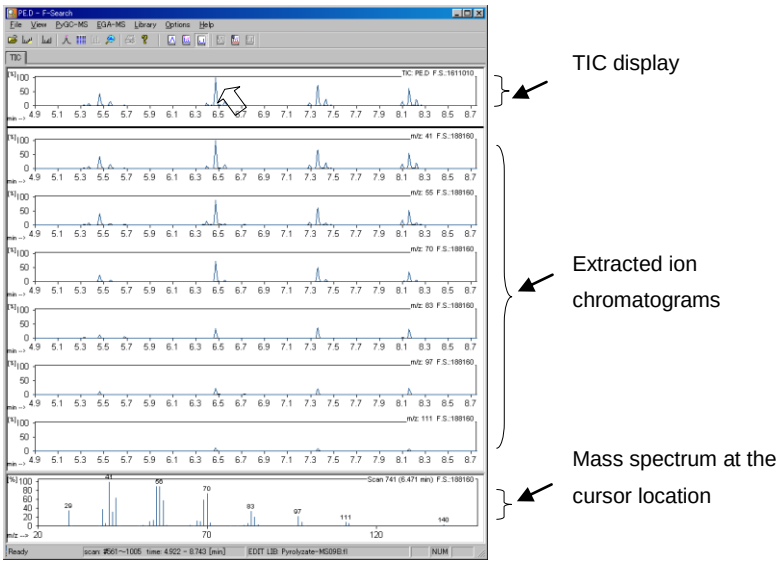


Fig. 5-8 Mass chromatograms

5.1.12 Two dimensional display of multi-ion mass chromatogram

This feature allows you to view two-dimensional mass chromatogram of ions (m/z) with a specified intensity or greater in a specified mass number range. From the menu bar, select [View] – [Mass Chromatograms…] to display a window shown in Fig. 5-9 where mass number range and minimum peak intensities that are displayed are entered. With this feature, you can easily find out whether or not a single peak on a TIC may actually be overlapped multiple peaks. Fig. 5-10 shows a broad peak at retention time around 2.57 minutes is actually an overlapped peak with other. Also, the background subtraction helps obtain high quality mass spectra, resulting in more accurate search results.

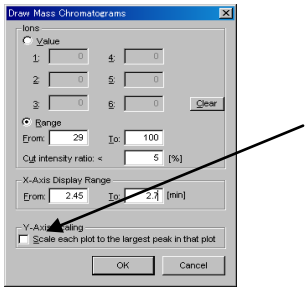
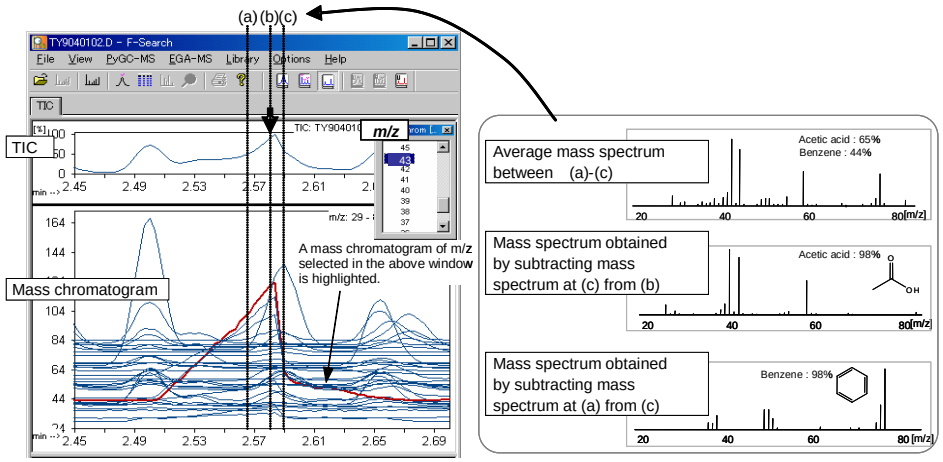


Fig. 5-9 Setting parameters for two-dimensional mass chromatogram

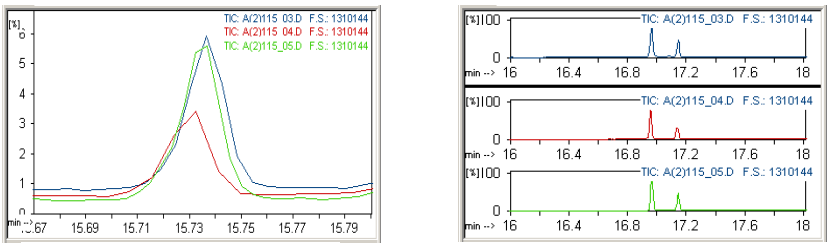


(a) Screen display (b) Search results using Pyrolyzate -MS library

Fig. 5-10 Two-dimensional display of multi-ion mass chromatograms

5.1.13 Overlay display of multiple TICs

Up to a maximum of seven TICs can be displayed overlaid in the same window. Go to the menu bar, and select [View] – [Overlayed TIC], and select MS data files to be overlaid. This will display chromatograms in merged format as shown in Fig. 5-11(a). To draw chromatograms separately as shown in Fig. 5-11(b), pull down [View] menu and uncheck [Merged Format].



(a) Overlay display of TICs (b) Separate display of TICs

Fig. 5-11 TICs for comparison

5.1.14 Subtracting a mass spectrum from a chromatogram (TIC)

A subtraction can be done to eliminate background or interfering peaks from a TIC.

(1) Subtracting a mass spectrum at any point of a TIC

Double-clicking the right-mouse button at any point of a chromatogram in a window

generates a mass spectrum in the mass spectrum window. Then from the menu bar, select [File] – [Subtract Background] to display the subtracted TIC. The new data file is saved in the SB folder (newly created if not present) under the MS data folder.

(2) Subtracting specified masses from a chromatogram (TIC)

Go to the menu bar and select [File] - [Subtract Ions], a dialog box is displayed, where up to six ions (m/z) and their abundances can be specified. Hitting OK button will display the subtracted TIC in the window. The subtracted TIC data is saved in the SB folder (newly created if not present) under the MS data file folder.

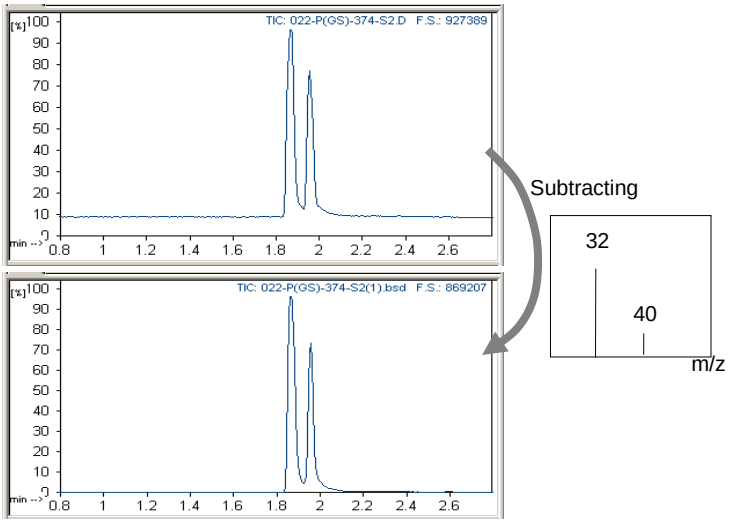


Fig. 5-12 Subtracting specified masses from a TIC

5.1.15 Selecting libraries

Data sources, library types, search targets, and filenames for each Frontier Laboratories library are shown in Table. 5.1. Which library to use depends on your search target. There are three types of libraries that are categorized according to how the mass spectra were obtained. They are EGA (see section 5.2), Int-Sum (section 5.3), and Compound (section 5.4). A user library must fall into one of these library types. All the Frontier Laboratories libraries in the F-Search folder (default location is C:\Program Files\FSearch) are automatically loaded when F-Search starts up. On the other hand, a user library must be specified in order to use it. Go to the menu bar and select [Library] – [Select Libraries for Search], then add check marks on the user libraries (if any) you would like to use for your search (Fig. 5-13). Only checked libraries are searched. Libraries can also be selected from the tool bar buttons as shown in Fig. 5-14.
Note that libraries with different library types (e.g. EGA and Int-Sum) cannot be selected simultaneously.

Table. 5.1 Frontier Laboratories libraries selection

Data source	Type of library	Search target	Library filename
Evolved gas analysis (EGA-MS)	EGA	Polymeric materials	EGA-MS14B.fl
Pyrolysis GC/MS (Py-GC/MS)	Int-Sum	Polymeric materials	PyGC-MS14B.fl
Reactive pyrolysis GC/MS (THM-GC/MS)	Int-Sum	Polymeric materials	PyGC-MS14B.fl
Pyrolysis GC/MS (Py-GC/MS)	Compound	Pyrolyzates of polymeric materials	Pyrolyzate-MS13B.fl
Reactive pyrolysis GC/MS (THM-GC/MS)	Compound	Pyrolyzates of polymeric materials	Pyrolyzate-MS13B.fl
Pyrolysis GC/MS (Py-GC/MS)	Compound	Additives	ADD-MS16B.fl
Thermal desorption GC/MS (TD-GC/MS)	Compound	Volatiles (Impurities, additives, residues, etc.)	ADD-MS16B.fl

Table. 5.2 Type of libraries

Type of library	Source of Mass spectra
EGA	Average mass spectra from EGA thermograms
Int-Sum	Integration summation (Int-Sum) of pyrograms
Compound	Each peak on pyrograms

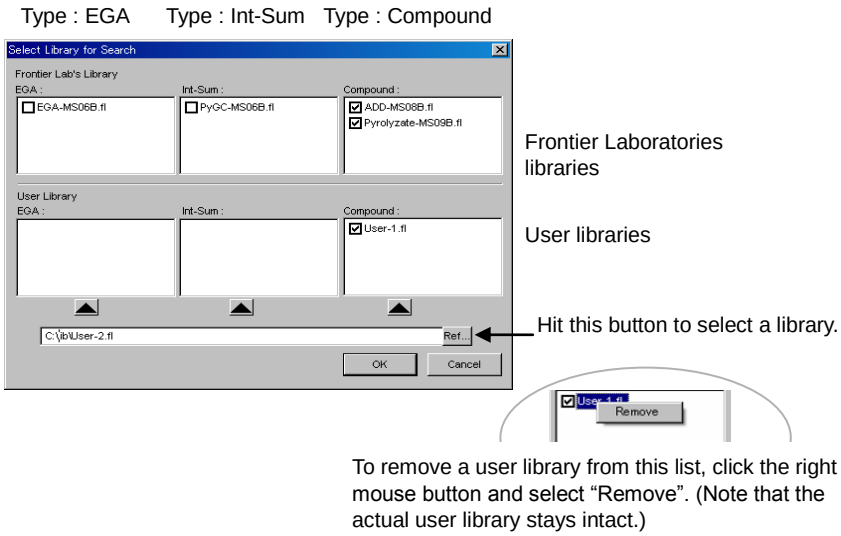


Fig. 5-13 Selecting libraries for search

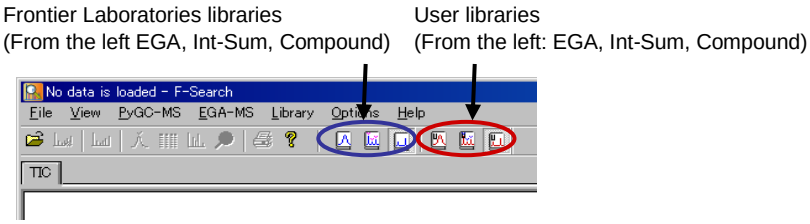


Fig. 5-14 Selecting libraries for search from the tool bar

5.1.16 Library search

How to generate a mass spectrum depends on the library being used. Detailed descriptions are found in sections 5.2 -5.5 . A simple search example is shown in Fig. 5.14. If a search is executed, a tab “Search” is created, and 100 candidate compounds are listed in the descending order of match quality [Qual], with the highest on the top of the list. The mass spectrum of an unknown compound is displayed at the top of the window, and the mass spectrum of the candidate compounds are displayed in the middle of the window. The match quality can also be visually examined by switching between chromatogram and thermogram views.

Each candidate mass spectrum or chromatogram/thermogram can be displayed by left-clicking any entry in the list of search results shown at the bottom of the window. Listings can be sorted by clicking the column header, either in descending order or in

ascending order.

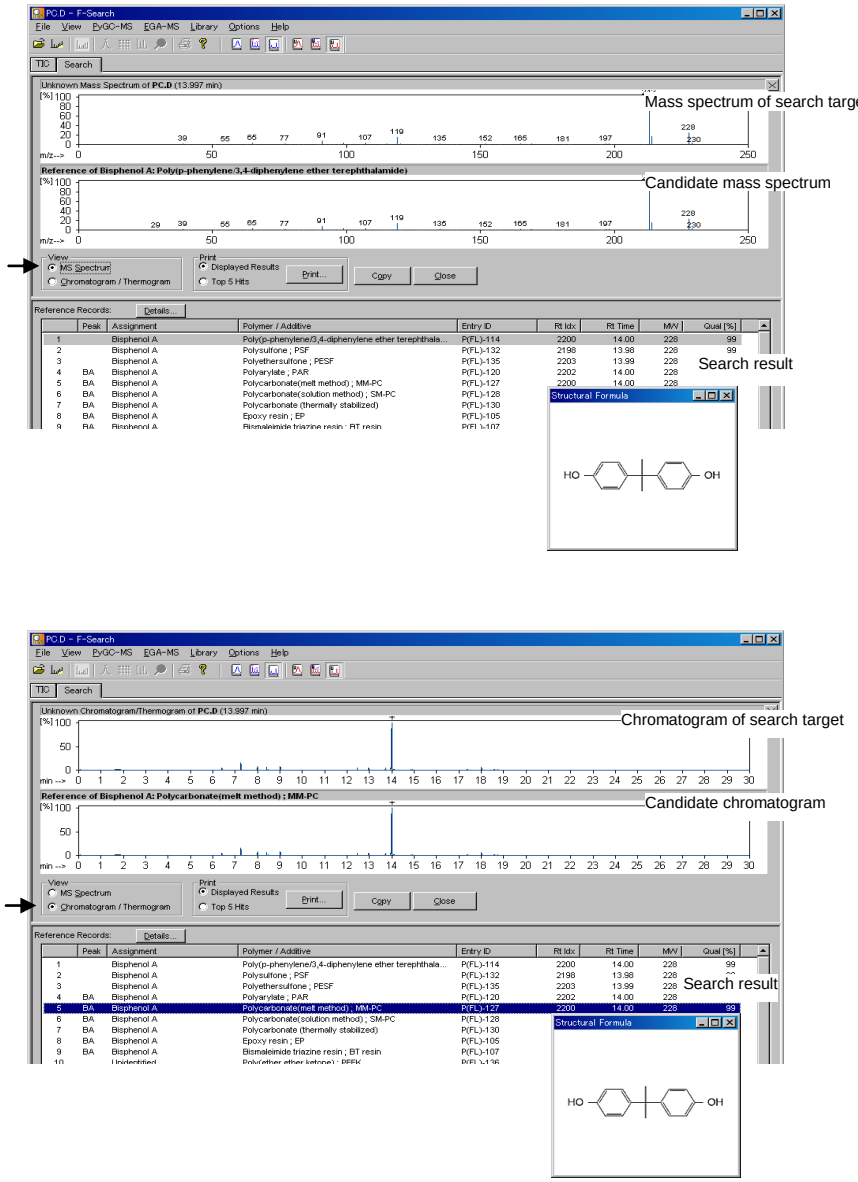


Fig. 5-15 Viewing search results

5.1.17 Printing the search results

Select [Displayed Results] and click [Print...] in the search results window to print the two charts that are displayed (mass spectrum or chromatogram) and the listings of search results.

5.1.18 Printing the search results in a report format

Select [Top 5 Hits] and click [Print...] in the search results window to print a pyrogram and the top five library data in the search results listings (mass spectrum or chromatogram).

5.1.19 Copying the search results to the clipboard

Select [Copy] in the search results window to copy two charts that are currently displayed (mass spectrum or chromatogram) to the clipboard.

5.1.20 Viewing the search results in detail

Select [Details] in the search results window to display details of the candidate compounds that are selected in the search results listings (Fig. 5-16).

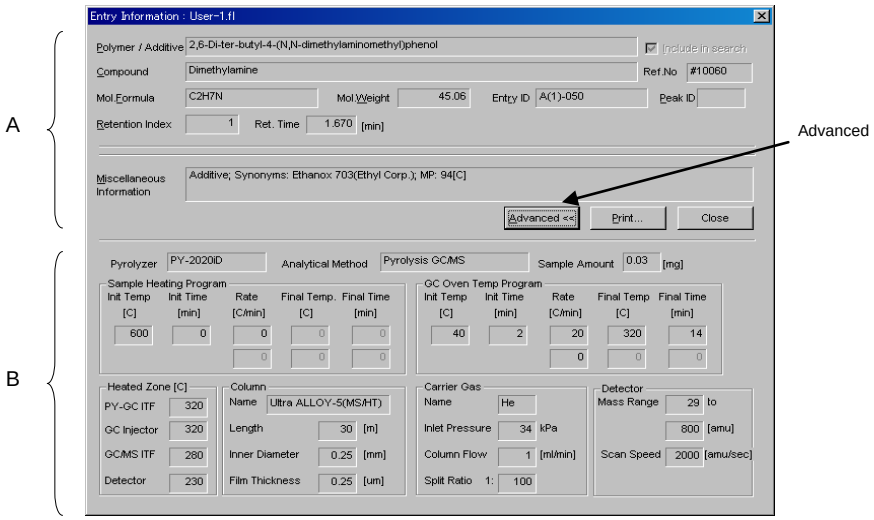


Fig. 5-16 Viewing candidate compounds in detail

(Clicking “Advanced” will expand the display (A & B), click it again to collapse (A))

5.2 Library search for polymers using EGA-MS library

Procedures for polymer library search using EGA data

(1) Open the mass spectral data file of interest.

(2) Select a library file. Normally EGA-MS14B.fl is selected.

(3) To label the horizontal axis with temperatures, Select [EGA-MS] - [Display

Temperature] from the menu bar. The dialog box shown in Fig. 5-17 will be displayed. Enter pyrolyzer temperature parameters and select [OK].

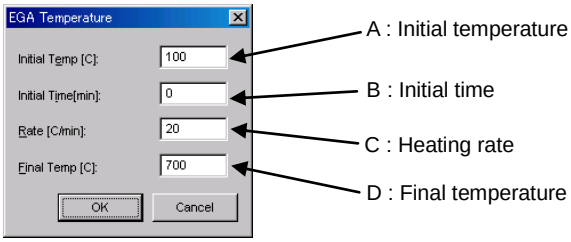


Fig. 5-17 Entering the temperature parameters for the EGA

(4) To create an average spectrum over any time range, select [EGA-MS] - [Make Mass Spectrum...]. The dialog box shown in Fig. 5-18 will be displayed. Fill the box with start time, end time, and the retention time of the background spectrum. Select [OK] to display an average mass spectrum over the specified time range. “Dragging” the cursor while holding the right-mouse button will also produce an average spectrum. (See section 5.1.4)

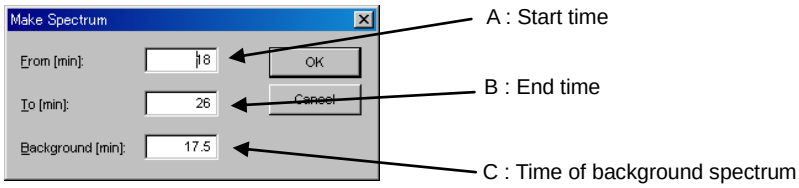


Fig. 5-18 Creating an average spectrum

(5) Select [EGA-MS] - [Search] from the menu. The search results shown in Fig. 5-19 will be displayed. Double clicking the right-mouse button on a mass spectrum window will produce the same results (see section 5.1.3).

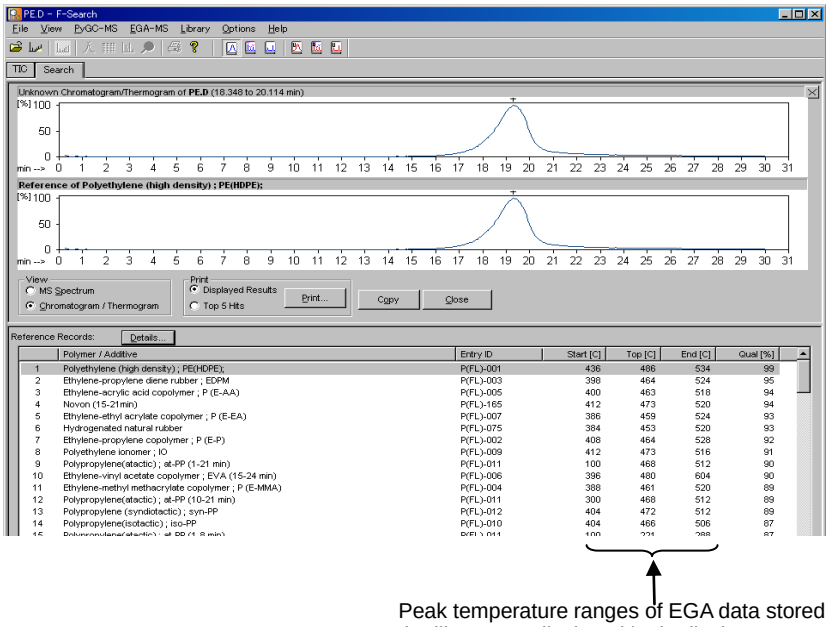


Fig. 5-19 Result of polymer search against EGA data

5.3 Library search for polymers using PyGC-MS library

Procedures for searching the polymer library Py-GC data are described.

(1) Open the mass spectral data file of interest.

(2) Select a library file. Normally PyGC-MS14B.fl is selected.

(3) Select [PyGC-MS] - [Detect Peaks] from the menu. The dialog box shown in Fig. 5-20 will be displayed. Enter the appropriate values for detecting each peak. In the case of a pyrogram obtained under standard Py-GC conditions, the default values are 2 [%] for intensity and 0.04 [min] for half-height peak width. Adjusting these values may be required for optimal peak integration. As shown in Fig. 5-21, clicking the [Add] button will display a dialog box where peak detection parameters are entered. This will override the settings previously entered - see Fig. 5-22. Customized peak integration parameters can be saved by selecting [Save]. To load a file, click [Load] then specify the file.

Clicking [OK] initiates the peak detection process and the results are displayed, as shown in Fig. 5-22. Peaks with a retention time are ‘detected’ peaks.

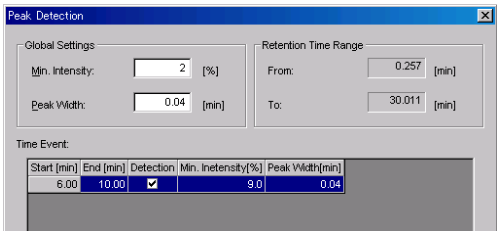


Fig. 5-20 Setting peak detection parameters

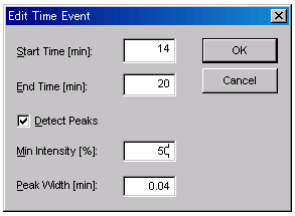


Fig. 5-21 Setting peak detection parameters for a specific time interval.

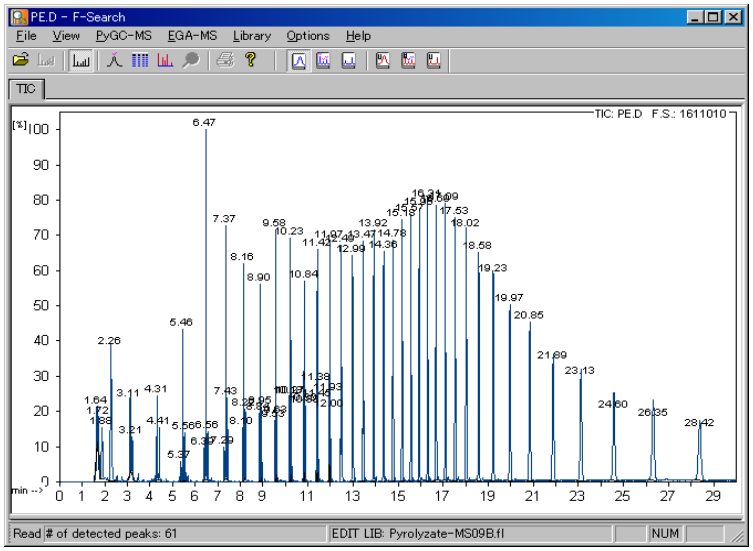


Fig. 5-22 Peak Detection

(4) Select [PyGC-MS] - [List Results] to display the total ion chromatogram and the retention times of all integrated peaks (Fig. 5-23). If undesired peaks are integrated, they can be deleted by selecting the row of that peak, followed by right-clicking to display a pop-up menu, select [Delete]. To insert a new peak right below the selected row, select [Insert] in the pop-up menu.

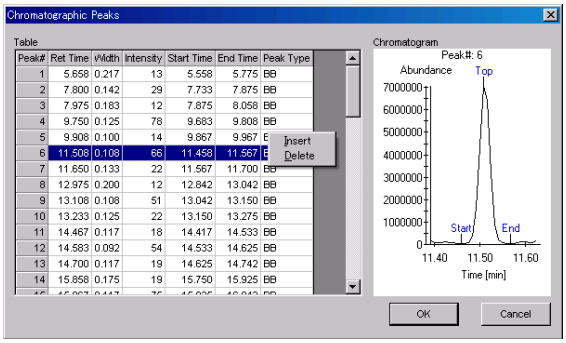


Fig. 5-23 Deleting and adding peaks

(5) Select [PyGC-MS] - [Make INT-SUM Mass Spectrum...], then specify the time range over which all peaks will be integrated. Select integration summation (INT-SUM). Select [OK] to generate an INT-SUM mass spectrum which is displayed at the bottom of the window as shown in Fig. 5-24.

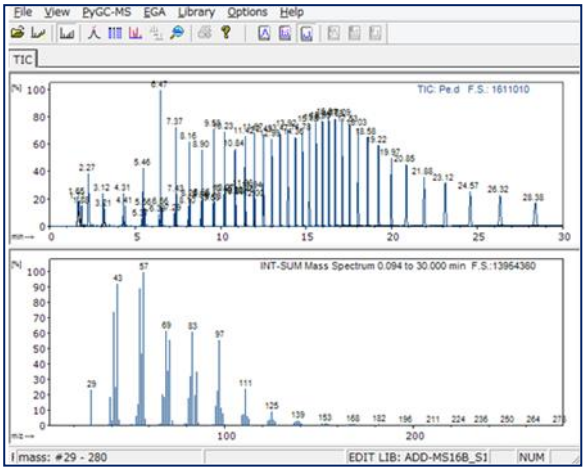


Fig. 5-24 INT-SUM mass spectrum

(6) The library search is performed against the INT-SUM spectrum just created using the library selected in Step 2. Select [PyGC-MS] - [Search] from the menu to view search results shown in Fig. 5-25. Double clicking the right-mouse button on a mass spectrum also produces the same results (see section 5.1.3).

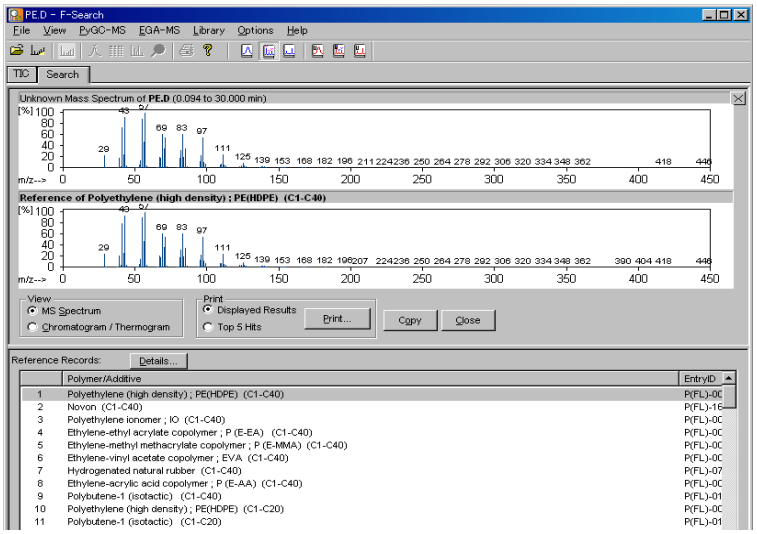


Fig. 5-25 Results of polymer search against Py-GC/MS data

5.4 Library search for additives using the ADD-MS library

The procedures for additive library search using Py-GC data are described.

(1) Open the mass spectral data file of interest.

(2) Select a library file. Normally ADD-MS16B.fl is selected.

(3) A mass spectrum is created from a total ion chromatogram which is then compared to spectra in the library. This is done by double-clicking the right-mouse button on the apex of a peak (see section 5.1.3), or by dragging the right-mouse button which selects the peaks over the desired time interval (see section 5.1.4). The mass spectrum of the single peak or the average mass spectrum is displayed at the bottom of the window.

(4) Double clicking the right-mouse button in a mass spectrum window initiates the library search, and search results are displayed as shown in Fig. 5-26. When using ADD-MS library, the molecular structure of selected candidate is shown in a small window as shown below.

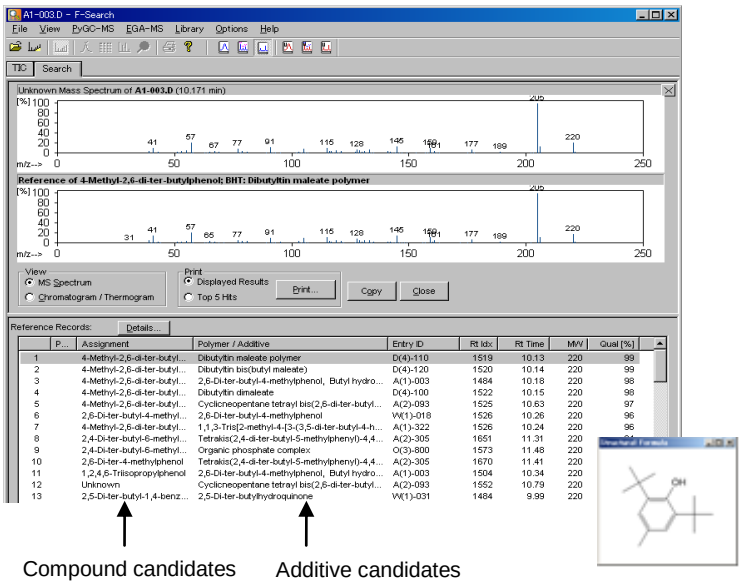


Fig. 5-26 Results of additives search against Py-GC/MS data

5.5 Library search for pyrolyzates using Pyrolyzate-MS library

Library search procedures for polymer pyrolyzates are described using data obtained by the Py-GC technique.

(1) Load a mass spectral data file to be searched.

(2) Select a library file for search, normally “Pyrolyzate-MS13B.fl” is selected.

(3) With the cursor at top of a peak, double-click the right mouse button (section 5.1.3), or drag the right mouse button across a peak over a time interval (5.1.4). The mass spectrum of the peak or the average mass spectrum is displayed at the bottom of the window.

(4) Double-clicking the right mouse button in the window where the mass spectrum is displayed initiates a library search. A typical search result is shown in Fig. 5-27. The Pyrolyzate-MS library, also displays the structure formula of selected candidates.

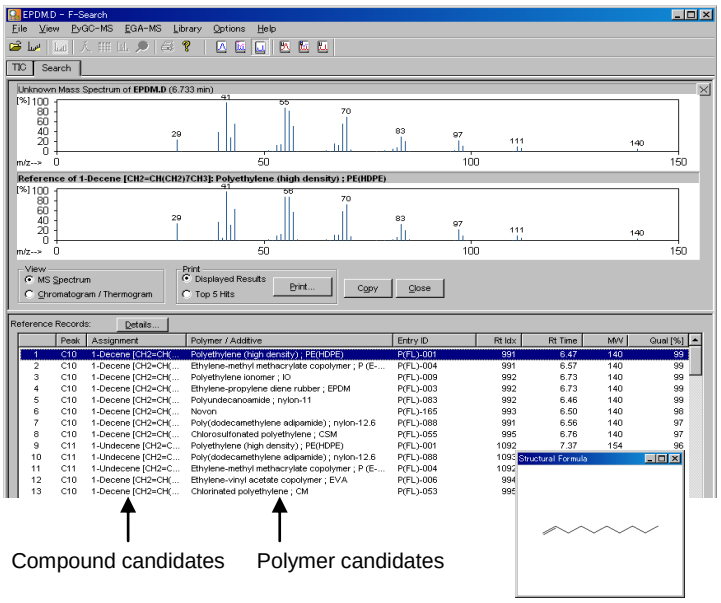


Fig. 5-27 Results of additive search against Py-GC/MS data

5.6 Creating and using a “user” library

You can create a custom library using thermograms and chromatograms that you have obtained. However, you can not edit libraries purchased from Frontier Laboratories.

5.6.1 Creating a new “user” library

From the menu bar, select [Library] - [Create...]. Enter a filename for the new library, and click [Save]. Enter information in the dialog box - Fig. 5-28, and select [OK]. The information entered in this library can be edited any time by going to [Library] - [Edit library Header...]. Once a library has been created, it remains active.

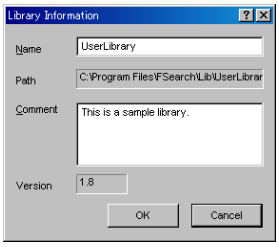


Fig. 5-28 Entering information for a new library

5.6.2 Entering EGA-MS data into a user library

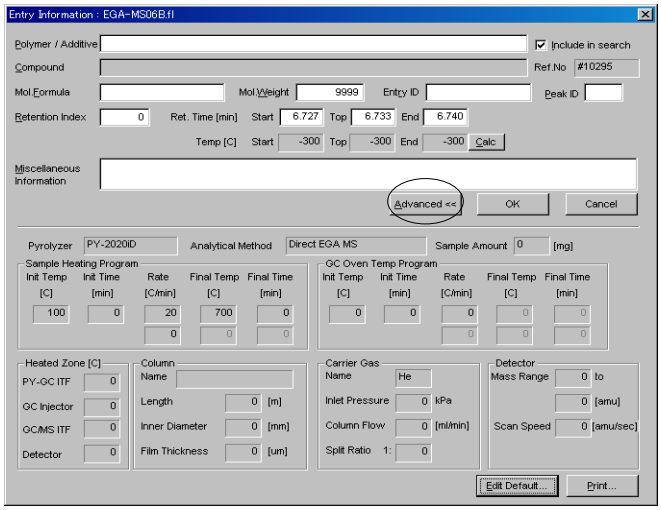
(1) Create an average mass spectrum from the thermogram obtained by EGA-MS (see

section 5.2).

(2) From the menu, select [Library] - [Add New Entry]. When entering the first mass spectrum from the EGA-MS data into the library, the dialog box shown in Fig. 5-29(a) is displayed. The analytical conditions are entered. When entering additional mass spectra, a simplified dialog box, shown in Fig. 5-29(b), is displayed, Clicking [Advanced] will display the complete dialog box so that the analytical conditions can be added.

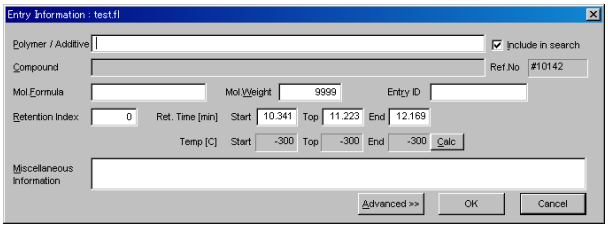
(3) By selecting [Edit Default...] the analytical conditions shown in Fig. 5-30 can be edited. For EGA data, be sure to select "Direct EGA-MS" from the pull-down menu under “Analytical Method”. After entering the temperature settings (for the pyrolyzer, GC, and interface), the type of column, and the mass spectrometer conditions, select [OK]. Note that the information entered here can be edited at any time (see section 5.6.6 for details).

(4) Enter the sample information, see Fig. 5-31. Selecting [Calc] allows the temperature range for the mass spectrum to be set according to the time interval of the average mass spectrum. Note that this requires that the temperature settings for the pyrolyzer be entered in advance. Table. 5.3 shows the various field names. Press [OK] to complete the process. The information entered here can be modified at any time (see section 5.6.6 for details).



Expanded by clicking "Advanced" button

(a) Dialog box for entering the first mass spectrum from EGA-MS data



(b) Dialog box for entering the subsequent mass spectra from any chromatogram

Fig. 5-29 Dialog box for entering the mass spectra

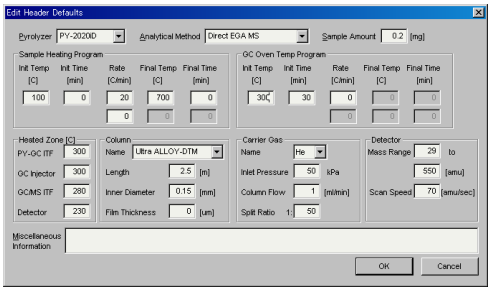


Fig. 5-30 Entering analytical conditions used for EGA

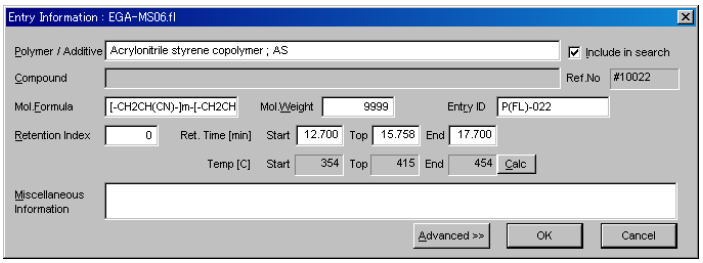


Fig. 5-31 Entering information about a polymer sample

Table. 5.3 Description of each field in the EGA data entry dialog box

Field label	Description
Polymer/Additive	Sample name
Mol. Formula	Molecular formula
Mol. Weight	Molecular weight (9999 for polymers)
Entry ID	Character strings entered for your sample classification
Peak ID	Character strings entered for your peak classification
Ref. No	Unique sequential number assigned to each record in library starting at 10000
Include in search	Uncheck to exclude from search
Retention Index	Defaulted to 0 for EGA
Ret. Time	Time range on EGA profile from which average mass spectrum was created
Temp	Temperature range on EGA profile from which average mass spectrum was created
Misc. Information	Additional information

5.6.3 Entering data from the polymer pyrogram into a “user” library (conversion to an Int-Sum spectrum and data entry)

(1) Create an "INT-SUM" mass spectrum from the pyrogram by using the integration-summation technique (see section 5.3).

(2) From the menu, select [Library] -[Add New Entry]. When entering the first mass spectrum from the pyrogram, the dialog box shown in Fig. 5-29(a) is displayed. When entering the second and subsequent mass spectra, a simplified dialog box - see Fig. 5-29(b), is displayed. Clicking [Advanced] will display the full dialog box.

(3) The analytical conditions can be edited by selecting [Edit Default...] see Fig. 5-28.

After entering the temperature settings (for the pyrolyzer, GC, and interface), the type of column, and the mass spectrometer conditions, press [OK]. Note that the information entered here can be edited at any time (see section 5.6.6 for details).

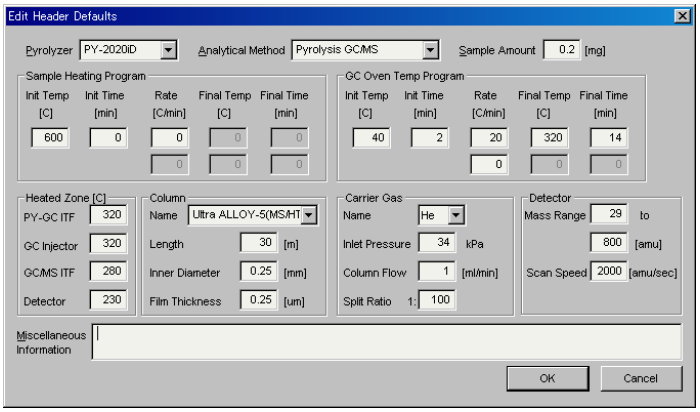


Fig. 5-32 Entering analytical conditions for Py-GC/MS analysis

(4) Enter the sample information shown in Fig. 5-33. Table. 5.4 describes each field. Click [OK] to complete this process. Note that information entered can be edited at any time (see section 5.6.6 for details).

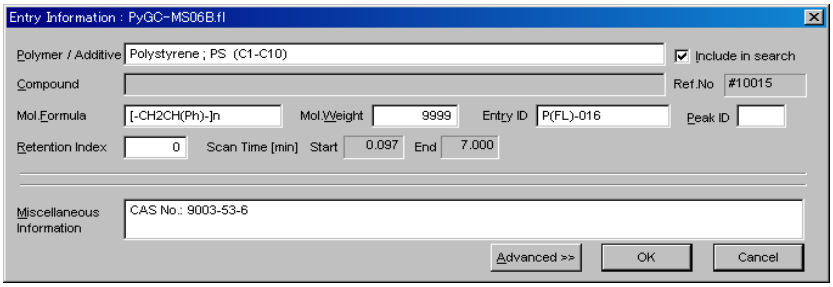


Fig. 5-33 Entering INT-SUM spectral data for a sample

Table. 5.4 Field descriptions for the INT-SUM spectral data entry dialog box

Field label	Description
Polymer/Additive	Sample name
Mol. Formula	Molecular formula
Mol. Weight	Molecular weight (9999 for polymers)
Entry ID	Character strings entered for your sample classification
Peak ID	Character strings entered for your peak classification
Ref. No	Unique sequential number assigned to each record in library starting at 10000

Include in search	Uncheck to exclude from search
Retention Index	Retention index, defaulted to 0 for INT-SUM mass spectrum
Scan Time	Time range of pyrogram from which INT-SUM mass spectrum was created
Misc. Information	Additional information

5.6.4 Entering additive data into a “user” library

(1) Create a mass spectrum from the analytical data obtained by Py-GC/MS or Thermal Desorption-GC/MS (see section 5.4).

(2) From the menu, select [Library] - [Add New Entry]. When entering the first mass spectrum from the pyrogram, the dialog box shown in Fig. 5-29(a) is displayed. When entering subsequent mass spectra, the simplified dialog, shown in Fig. 5-29(b), is displayed. Clicking [Advanced] will display the complete dialog box.

(3) Clicking [Edit Default...] allows you to edit the analytical conditions as shown in Fig. 5-34. After entering temperature settings (for the pyrolyzer, GC, and interface), the type of column, and the mass spectrometer conditions, press [OK]. Note that the information entered can be edited at any time (see section 5.6.6 for details).

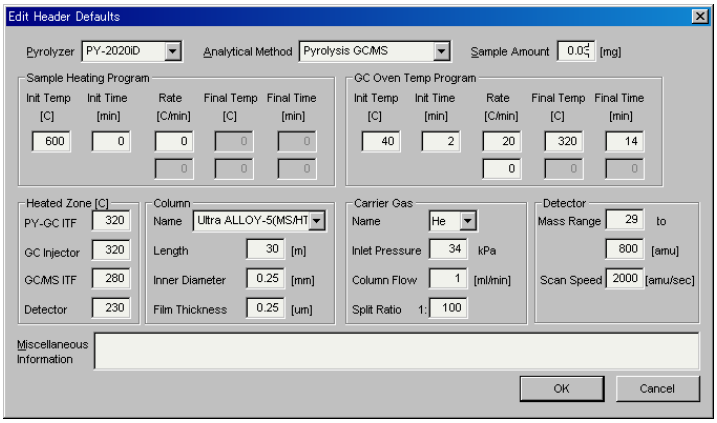


Fig. 5-34 Entering analytical conditions for the Py-GC/MS data

(4) Enter the sample information as shown in Fig. 5-35. Table. 5.1 describes each field. Click [OK] to complete this process. Note that information entered can be edited at any time (see section 5.6.6 for details).

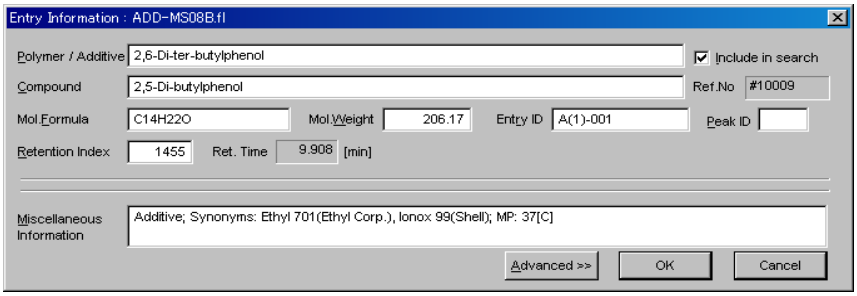


Fig. 5-35 Entering Py-GC/MS data for an additive sample

Table. 5.5 Field descriptions for Additive Py-GC/MS data entry dialog box

Field label	Description
Polymer/Additive	Additive name
Compound	Compound name
Mol. Formula	Molecular formula
Mol. Weight	Molecular weight (9999 for polymers)
Entry ID	Character strings entered for your sample classification
Peak ID	Character strings entered for your peak classification
Ref. No	Unique sequential number assigned to each record in library starting at 10000
Include in search	Uncheck to exclude from search
Retention Index	Retention index, defaulted to 0
Ret. Time	Retention time on pyrogram from which mass spectrum was created
Misc. Information	Additional information

5.6.5 Entering pyrolyzate data for a polymer to a “user” library

(1) Create a mass spectrum from a pyrogram obtained by the Py-GC analysis of a polymer (see section 5.4).

(2) From the menu bar, select [Library] - [Add New Entry…]. When entering the first mass spectrum from the pyrogram, the dialog box shown in Fig. 5-29(a) is displayed. Enter the analytical conditions. When entering the second and subsequent mass spectra, a simplified dialog box, Fig. 5-29(b) is displayed. Click [Advanced] to display all analytical conditions.

(3) Clicking [Edit Default…] allows you to edit the analytical conditions as shown in Fig. 5-36. After entering the temperature settings (for pyrolyzer, GC, and interface), type of

column, MS analytical conditions, select [OK]. Note that the information entered can be edited at any time (see section 5.6.6).

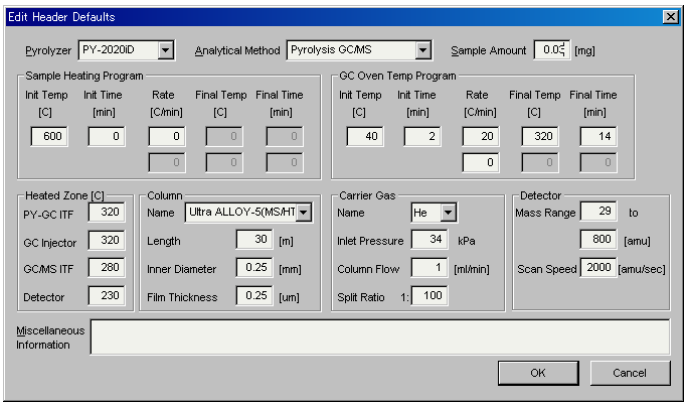


Fig. 5-36 Entering analytical conditions for Py-GC/MS analysis

(4) As shown in Fig. 5-37, enter the sample information. Table. 5.1 describes each field. Click [OK] to complete this process. Note that the information entered here can be edited any time (see section 5.6.6). Repeat steps 1 through 4 above to add multiple records to the library.

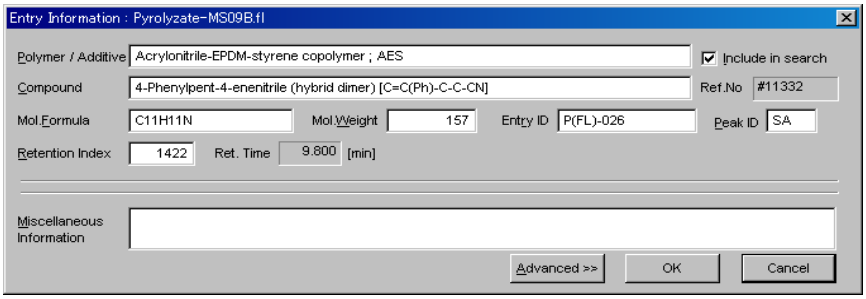


Fig. 5-37 Entering Py-GC/MS data of polymer pyrolyzates

Table. 5.6 Field description for Py-GC/MS data of polymer pyrolyzates

Field label	Description
Polymer/Additive	Polymer name
Compound	Compound name
Mol. Formula	Molecular formula
Mol. Weight	Molecular weight (9999 for polymers)
Entry ID	Character strings entered for your sample classification
Peak ID	Character strings entered for your peak classification

Ref. No	Unique sequential number assigned to each record in library starting at 10000
Include in search	Uncheck to exclude from search
Retention Index	Defaulted to 0
Ret. Time	Retention time on pyrogram from which mass spectrum was created
Misc. Information	Additional information

5.6.6 Viewing and editing library data

(1) From the menu, select [Edit Existing Entry...] or [View Existing Entry…] (If you use a protected library, you can only view the library data). The list of entries, shown in Fig. 5-38, will be displayed.

(2) If the spectra stored in the library are (1) mass spectra created from GC chromatograms or from thermograms obtained via the evolved gas technique, a list of entries will be displayed by selecting [Compound]. (2) if the spectra stored in the library are INT-SUM mass spectra created using the integration-summation from a pyrogram, the entry list is displayed by selecting [Int-Sum].

(3) To edit entries stored in the library, click [Edit]. Selecting [Advanced] displays the analytical conditions, while clicking [Edit Default..] allows you to edit the analytical conditions. See sections 5.6.2 and 5.6.3.

(4) To delete entries stored in the library, select the entry and click [Delete].

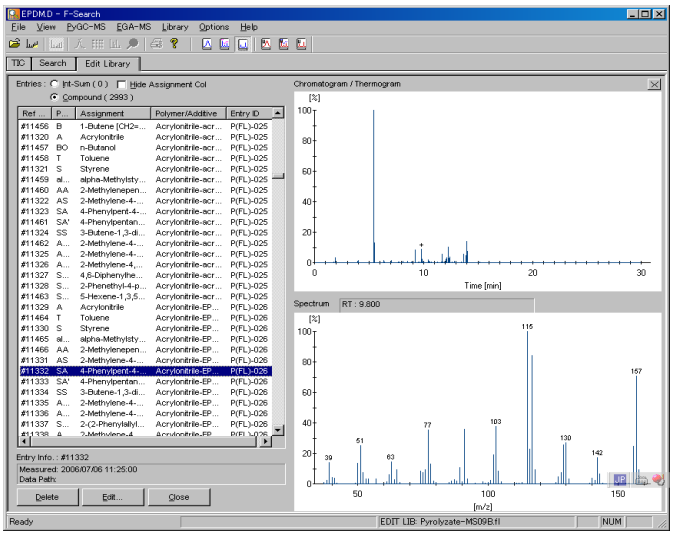


Fig. 5-38 Viewing and editing user library data

5.7 Library security

Libraries can be password-protected to prevent unauthorized modifications.

5.7.1 Setting a password for protection

From the menu bar, select [Library] - [Password Protection...]. The dialog box shown in Fig. 5-39 is displayed. Type a password in the "New Password“ and “Confirm New Password” fields. Press [Apply] to activate. Please note that if the password is lost or forgotten, there is no way to “unprotect” the libraries. Contact Frontier Laboratories either by email (cs@frontier-lab.com) or visit our website (http://www.frontier-lab.com) for assistance

To set a new password, type the current password in the "Current Password" field and enter the new password in the "New Password" and “Confirm New Password” fields, Press [Apply].

5.7.2 Unprotecting libraries

Type in your current password - see Fig. 5-40, in the "Current Password" prompt and leave the “New Password” field blank; click [Apply]. Library entries can now be edited. To re-protect the libraries, select a password and proceed as instructed above.

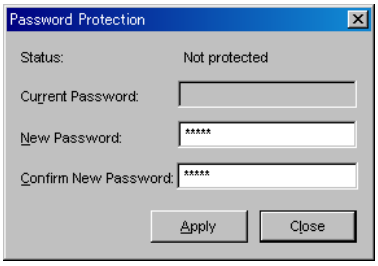


Fig. 5-39 Entering a password

Fig. 5-40 Removing protection

5.8 Searching the NIST library

If the NIST/EPA/NIH Mass Spectral Library and its search software have been installed on your PC, it can be used from within F-Search as shown in Fig. 5-41.

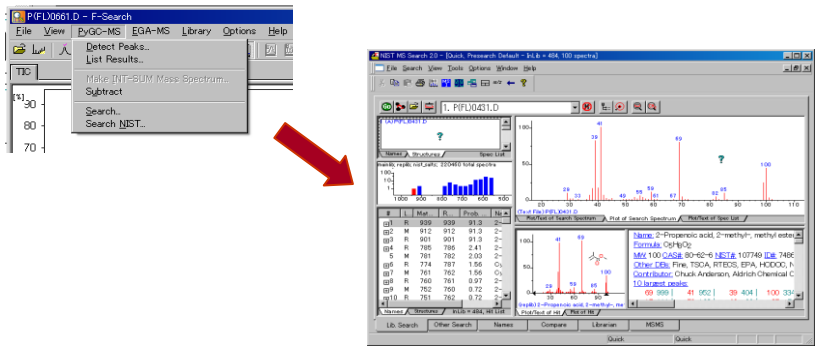


Fig. 5-41　NIST library search from within F-Search

Note :

If you do not have a write-privilege to the “autoimp.msd” file in the folder where the NIST library is installed (default location is C:\NISTxx\MSSEARCH). Access the NIST library from within F-Search. If the error message “Can not start NIST” is displayed, consult your system manager to obtain a write-privilege for “autoimp.msd” file.

CHAPTER 6 EVOLVED GAS ANALYSIS (EGA)

6.1 Flow configuration for Evolved Gas Analysis

Fig. 6-1 shows the gas flow configuration for performing evolved gas analysis (EGA). The sample is “dropped” into the “Multi-Shot” Pyrolyzer. The furnace temperature is programmed from a low to a higher temperature. As the sample is heated, vapors evolve. The vapors are swept through the split/splitless injection port. A fraction (e.g. 1/50) of the gases pass through the EGA capillary tube which is kept at 300 ºC to prevent condensation. The gases are “detected” by a mass spectrometer (MS). A plot of sample temperature v. detector response is called a ‘thermogram’.

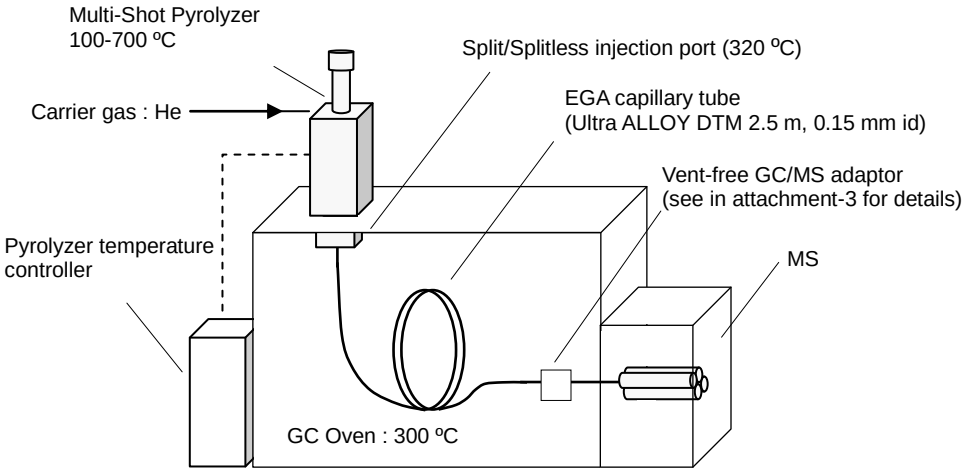


Fig. 6-1 Flow configuration for EGA

6.2 Analytical conditions for the EGA-MS library data

The data in the EGA-MS library has been produced using the analytical conditions described in section 6.2.1. These conditions yield the highest quality thermogram and mass spectral quality for the broadest range of polymers.

When analyzing unknowns or building a “user” library, slight differences in the initial temperature and/or flow rate have little effect on the resulting thermogram, when using the Frontier Laboratories pyrolyzer (Multi-Shot Pyrolyzer-model EGA/PY-3030D).

Note: If a non Frontier Laboratories pyrolyzer or TG-MS is used, the EGA thermogram may differ from those in the library due to active sites, dead space, or cool spots in the flow path. Care must be taken to prevent system overload. If this occurs, the EGA-library may produce results which have limited value.

6.2.1 Analytical conditions for Evolved Gas Analysis

A. Instruments

Pyrolyzer	: Multi-Shot Pyrolyzer (EGA/PY-3030D, Frontier Laboratories)
GC/MS	: Quadrupole GC/MS of Agilent, JEOL, Shimadzu and others
Interface (ITF)	: Deactivated metal capillary tube, 2.5 m, 0.15 mm id (Frontier Laboratories P/N: UADTM-2.5N)

B. Sample and sample cup

Amount of sample	: 0.1-0.3 mg
Sample form	: Film or powder
Sample cup	: Disposable Eco-Cup LF (80 µL, P/N: PY1-EC80F)
Sampler	: Auto-Shot sampler (P/N: AS-1020E) or Manual sampler

C. Temperature and flow conditions

PY

PY (sample) temp.	: 100ºC - 20 ºC/min - 700ºC
PY/GC ITF temp.	: 300ºC

GC

Oven temperature	: 300ºC
Injection port temp.	: 300ºC
GC/MS ITF temp.	: 280ºC
Carrier gas	: Helium
Split ratio	: 1/50
Column flow rate	: 1 mL/min

MS

Mass range	: m/z 29 - 550
Sampling rate	: 6 (0.13 scan/sec) The slow sampling rate is important in order to improve the S/N ratio.
Threshold level	: 200 counts
Multiplier	: Voltage set by Autotune

6.2.2 Notes on performing Evolved Gas Analysis

A. Sample preparation

With the EGA-MS technique, reproducibility is dependent upon both the amount and form of the sample. If a sample is soluble in an organic solvent, prepare a solution and place several microliters in the sample cup, evaporate the solvent; this leaves a film of the

sample on the inside surface of the cup. If the sample is insoluble, a small amount of powered sample can be used. The amount of sample used should be less than 0.3 mg.

If the sample is a solid mass and the shape varies from sample to sample, uniform heating of the sample cannot be established due to the low thermal conductivity of the sample matrix. This may reduce the reproducibility of the evolved gas curve (i.e., thermogram). If a solid sample is analyzed, the EGA curve may exhibit excess noise or a sudden rise of the baseline. This is due to the bumping of the compressed gases trapped in the solid matrix. If this occurs, reduce the amount of sample and/or use a film or pulverized sample as described below. Refer to attachment of technical notes of PYT-017E and PYT-018E.

There are four methods used to prepare a film or powder from a solid sample. Among these methods, methods A1), A2), and A3) are the simplest, however, methods A1), A2), and A4) generally yield the best results.

A1) Film method

The sample is dissolved in a solvent and a portion (e.g. 5µl) of the solution is placed in a sample cup. The solvent is evaporated; this results in a thin film in the sample cup surface. This method provides a uniformly thin film of the sample giving the best reproducibility. This method, however, cannot be applied to solvent insoluble polymers (e.g., thermosetting polymers).

A2) Use of "Polymer Prepper", a special pulverizing tool (by Frontier Laboratories)

The Polymer Prepper is a special tool which has minute grinding surfaces randomly formed on a nickel surface. It can be used to quickly pulverize a polymer sample into small particles of 0.1mm in diameter at ambient temperature. The polymer prepper has two grinding surfaces: fine and coarse. After use, the contaminated surface of the prepper can be cleaned by using a cleaning tape onto the surface. The prepper, however, cannot be used with soft and flexible materials such as rubber. If this is the case, use Methods A1) or A4).

A3) Cutter method

A sharp stainless steel blade can be used to cut a polymer sample into very small pieces. However, uniform particle sizes cannot be obtained, which may result in poor sample-to-sample reproducibility.

A4) Crushing with a metal ball in liquid nitrogen

The sample is frozen using liquid nitrogen and then crushed with a metal ball into powder.

Ensure that the sample is taken out of the container when the temperature is at room temperature to avoid condensation of moisture. Also, pyrograms may alter due to the contamination of metal particles from the metal ball.

B. Scan rate of EGA-MS

EGA peaks generally have gentle slopes, therefore, a scan rate of 1 scan/sec to 1 scan /10sec is usually adequate. Because noise is averaged using a low scan rate, EGA curves with a smooth baseline are obtained. EGA-MS data file are generally small, ranging from 100 to 300 KB.

When high scan rates are used as in the case of capillary column GC/MS, the EGA data file may be as large as 1MB and exhibit poor S/N.

C. Contaminations in continuous operation and effects to spectra

With use the pyrolyzer, GC injection port, PY-MS interface and MS ion source become contaminated. Maintenance is extremely important to order to obtain consistent, high quality mass spectra. Details are described in the following sections.

C1) Contaminations of the pyrolyzer

Generally the only points of contamination are the quartz pyrolysis tube and the interface needle between the pyrolyzer and GC injection port. Refer to the operation manual of the pyrolyzer for further details. The pyrolyzer is equipped with a 1/8 " copper tube at the split outlet. It must be replaced at least every 6 months.

C2) Contamination of the GC injection port

Contamination of the GC injection port liner depends on the frequency of analyses and the chemical composition of the samples; however, regular cleaning is required.

C3) Contamination of EGA capillary tube

The interface is a 2.5 m deactivated stainless steel capillary tube: Ultra ALLOY DTM. It connects the pyrolyzer and the MS. Although this capillary tube resists contamination, contamination does occur with extended use. The degree of contamination can not be determined by observing the background noise of the spectra. Solvents may remove high boiling contaminates; however, tars cannot be removed with solvents. When this occurs, the EGA tube must be replaced.

The recommended temperature for the interface is 300ºC; however, in order to reduce the contamination of the MS ion source, the interface temperature may be set to as low as

200ºC. If a low temperature is used, high boiling evolved gases may condense in the interface tube. We suggest that the analyst experimentally determine the optimum interface temperature.

C4) Contamination of the MS ion source

Generally, contamination of the ion source is caused by the deposition of column stationary phase and by the deposition of high boiling components originating from the pyrolysis of the sample. Bleeding from the deactivated EGA capillary tube should be negligible; therefore, contamination must come from the evolved gases.

When the ion source gets contaminated, it will result in abnormal spectra with a decreased in high mass ion intensities. This effect is even observed in PFTBA (perfluorotributylamine) spectra. If this effect is observed, clean the ion source.

CHAPTER 7 PYROLYSIS GC/MS (Py-GC/MS) ANALYSIS OF POLYMERS

7.1 Flow configuration for Py-GC/MS analysis

The sample is placed in a sample cup and positioned in the 'Multi-Shot" Pyrolyzer. It "free falls" into the center of the pyrolysis furnace which is at the pyrolysis temperature (600ºC). The sample is instantly pyrolyzed. Pyrolysis products are flushed through the split/splitless injection port by the carrier gas. The sample is split (by 1/10 to 1/100), a small amount of the sample is transferred to the analytical capillary column. The pyrolyzates are separated using temperature programmed, capillary column GC and analyzed by the mass spectrometer (MS).

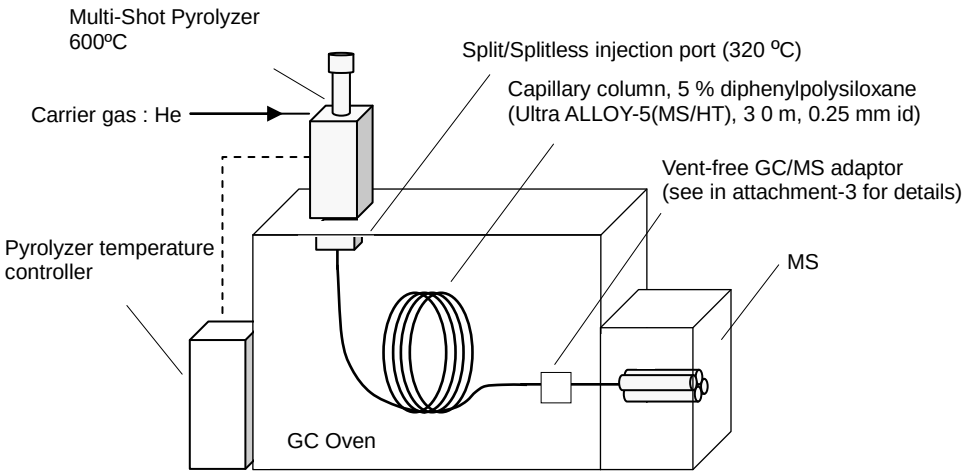


Fig. 7-1 Flow configuration for Py-GC/MS analysis

7.2 Analytical conditions for the data included in the PyGC-MS and Pyrolyzate-MS libraries

The data contained in the PyGC-MS and the Pyrolyzate-MS libraries has been obtained using the analytical conditions described in section 7.2.1. The analytical conditions were selected based on years of optimization work performed by the research staff at Frontier Laboratories.

One of the features of the PyGC-MS library is that, when analyzing unknowns or building a "user" library, small differences in the initial temperature and/or flow rate used do not effect the search results. The integration-summation (Int-Sum) search algorithm allows for fluctuations in the retention times.

7.2.1 Analytical conditions for the PyGC-MS method (an example)

A. Instruments

Pyrolyzer	: Multi-Shot Pyrolyzer (EGA/PY-3030D, Frontier Laboratories)
GC/MS	: Quadrupole GC/MS of Agilent, JEOL, Shimadzu and others
Column	: Ultra ALLOY-5 (5 % diphenyldimethylpolysiloxane) L=30 m, id=0.25 mm, 0.25 µm film thickness (MS/HT) (P/N: UA5(MS/HT)-30M-0.25F, Frontier Laboratories)

B. Sample and sample cup

Amount of sample	: approx. 0.1 mg
Sample form	: Powder (using Polymer Prepper described in CHAPTER 6)
Sample cup	: Disposable Eco-Cup LF (80 µL, P/N: PY1-EC80F)
Sampler	: Double-Shot or Single-Shot sampler or Auto-Shot sampler

C. Temperature and flow conditions

PY

PY temperature	: 600ºC
PY/GC ITF temp.	: 300ºC

GC

Oven temperature	: 40ºC(2 min hold) - 320 ºC(20 ºC/min, 14 min hold)
Injection port temp.	: 300ºC
GC/MS ITF temp.	: 280ºC
Carrier gas	: Helium
Split ratio	: 1/100
Column flow rate	: 1 mL/min

MS

Mass range	: m/z 29 - 550
Sampling rate	: 2 (3 scans/sec)
Threshold level	: 200 counts
Multiplier	: 200 V below the voltage set by Autotune

7.2.2 Notes on acquiring pyrograms

A. Sample preparation (contents are the same as section 6.2.2. for EGA-MS)

When using the Py-GC/MS technique, the amount and form of the sample is very important. If the sample is soluble in an organic solvent, prepare a quantitative solution and place micro liter quantities in a sample cup. Evaporate the solvent. This leaves a thin film of sample on the inside surface of the cup. If the sample is insoluble, a small amount of powered sample can be used. The amount of sample should be less than 0.1 mg.
If the sample is a solid mass or particles and the shape varies from sample to sample, uniform heating of the sample cannot be achieved due to the low thermal conductivity of the sample. This reduces the reproducibility of the pyrograms. If this is the case, reduce the amount of sample being analyzed and use a film or pulverized sample.
There are four methods commonly used to prepare a film or powder from a solid sample. Among these, methods A1), A2), and A3) are the simplest; however, methods A1) and A2) are the best for obtaining a high level of reproducibility.

A1) Film method

A known amount of sample is dissolved in a known volume of solvent. A portion of the solution is placed in a sample cup. The solvent is evaporated which results in a thin film on the surface of the sample cup. The method provides a uniformly thin film of the sample which yields the best reproducibility.

A2) Use of the polymer prepper, a special pulverizing tool (by Frontier Laboratories)

A polymer prepper is a special tool which has minute grinding surfaces randomly formed on a nickel thin film. It can be used to quickly pulverize a polymer into small particles, e.g., 0.1mm in diameter at ambient temperature. The polymer prepper has two grinding surfaces: fine and coarse. After use, the contaminated surface of the prepper can be cleaned by using a cleaning tape. The prepper cannot be used with soft and flexible materials such as rubber. In this case, use Methods A1) or A4).

A3) Cutter method

A sharp stainless steel blade can be used to cut a polymer into very small pieces. However, uniform particle sizes cannot be obtained, which may result in poor sample-to-sample reproducibility.

A4) Crushing with a metal ball in liquid nitrogen (i.e., cryo-milling)

The sample is frozen using liquid nitrogen and then crushed with a metal ball into powder.

B. MS scan rate

Capillary column peaks separated are often quite narrow; therefore, a scan rate of several scans/sec is usually required. If the analysis time is about 30 min, the disk space required may exceed 1.4 MB. If higher scan rates, e.g., tens of scans/sec, are used, the memory needed may be over 10 MB. The required memory space depends on the scan rate, scan range, and peak detection threshold. High scan rates produce high-quality chromatograms; When using this software, PyGC-MS LIB, a scan rate of several scans/sec is needed for satisfactory search results.

C. MS scan range

The scan range stored in the library is 29 to 550 amu. This range is acceptable for most applications; however, if the system is free of air, the scan should start at 10 amu. If there is air in the system or if the low mass region is not required, the initial scan can be set higher, e.g.,50 amu. In this case, the final TIC (Total Ion Chromatogram) and the averaged mass spectrum, based on the TIC, may be different which could result in poor matching ratios with the library.

The following guidelines can be used to determine the initial scan mass number:

Scan start mass number

10 -	: Ideal starting range
29 -	: Use if the air background (N2: 28, O2: 32) is low and can be ignored. On some instruments, background may be subtracted from the data set, even if the initial scan is 10 amu.
50 -	: Use if the water, air, and CO2 background can be ignored.

The highest scan mass number for most routine work is normally around 550; however, when analyzing bromine containing compounds, it should be increased to 1,000 amu.

D. Spectral pattern by Autotune

Many of the mass spectrometers available today, use the Autotune software to minimize spectral changes caused by ion source contamination. The best parameters for an analysis are automatically determined by the software, and are usually used for normal GC/MS operation. However, the detector voltage determined by Autotune is generally too high for Py/GC/MS. The reason is that the major components of pyrolysis are hydrogen chloride and carbon dioxide, or monomers of the depolymerizable polymers. High concentrations of these species often saturate the MS detector and dominate the resulting spectrum. In cases like this, the match quality generated by the library search may be adversely affected. To avoid this situation during the normal acquisition of pyrograms, the detector voltage

should be set 200V lower than the one set by the Autotune software.

E. Measures to prevent abnormal peaks in the pyrogram

Abnormal peaks are sometimes observed in the pyrogram of a sample. Such peaks often originate during the thermal decomposition of the column stationary phase or the thermal decomposition of the injection port septum. When the mass spectra of the GC peaks contain ions 73 and 207, it is a clear indication of septum bleed. The septum must be replaced.

If the sample cups are handled during sample preparation, spurious peaks such as squalene or cholesterol may be observed in the pyrogram. Use clean forceps to handle the sample cups. Fig. 7-2 shows an example in which the sample cup was handled with bare hands during sample preparation. These squalene peaks do not originate from the sample.

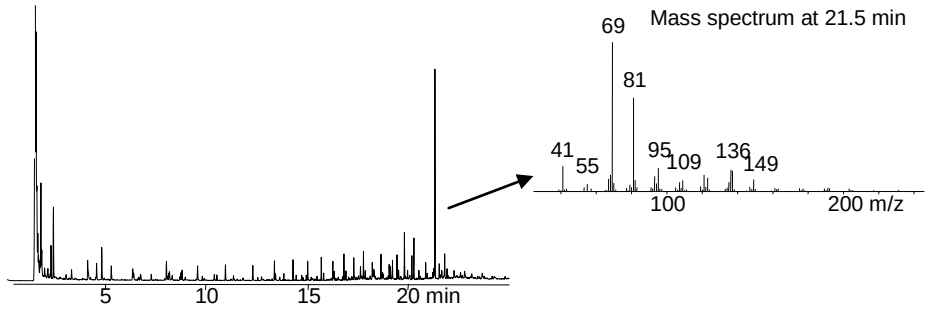


Fig. 7-2 Pyrogram of polycarbonate contaminated by squalene

F. Contamination resulting from continuous operation and its effect on spectral quality

During continuous Py-GC/MS analysis, the pyrolyzer (quartz pyrolysis tube and interface needle), GC injection port, GC capillary column and MS ion source may be contaminated. Regular maintenance of these areas is highly recommended. Details are described below.

F1) Contamination of the pyrolyzer

Generally the only points of contamination are the quartz pyrolysis tube and the interface needle between the pyrolyzer and GC injection port. Refer to the operation manual of the pyrolyzer for further details. The pyrolyzer is equipped with a 1/8 " copper line at the split outlet. It must be replaced at least every 6 months.

F2) Contamination of GC injection port

Contamination of the GC injection port liner depends on the frequency of analyses and the

chemical composition of the samples; however, regular cleaning is required. Install a 30 cm length of a 1/8" id copper tubing at the GC split outlet. It must be replaced every 6 months.

F3) Contamination of MS ion source

Generally, contamination of the ion source is caused by the deposition of high boiling components of the samples and/or fragments from the column's stationary phase.

Ion source contamination results in abnormal spectra in which the intensities of the high mass ions are reduced. Even the spectra of PFTBA (perfluorotributylamine) are affected. If this is observed, the ion source must be cleaned.

CHAPTER 8 Analysis of polymers using THM-GC/MS

8.1 Flow configuration of THM-GC/MS

The instrumentation for THM-GC/MS is shown in Fig. 8.1. Tetramethylammonium hydroxide, a methylating agent, is added to a sample cup containing a sample. The cup was loaded onto a Multi-Shot Pyrolyzer and was dropped (free fall) into the center of the furnace set at 400ºC for instant reactive pyrolysis. Pyrolyzates formed are introduced into the split/splitless injector of GC, split by a ratio ranging from 1/10 to 1/100, then are introduced into a separation column, and separated in a programmed temperature mode. Lastly, they are detected by a mass spectrometer (MS).

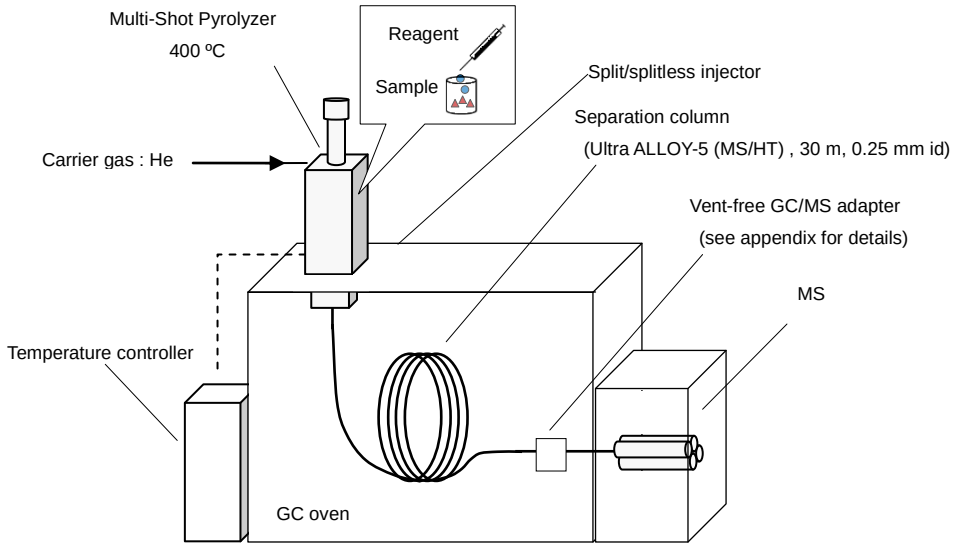


Fig. 8.1 Instrument configuration for Py-GC/MS

8.2 Analytical conditions used for PyGC-MS library and Pyrolyzate-MS library

These two libraries were constructed using the analytical conditions shown in section 7.2.1. The conditions have been developed by Frontier Laboratories' research and development staff upon many years of extensive research.

The PyGC-MS library is featured by integration-summation algorism (INT-SUM) which is virtually not affected by variations of factors such as initial temperature, column flow rate, retention time, etc. when analyzing unknowns or constructing a library.

8.2.1 PyGC-MS analytical conditions (example)

A. Instrument

Pyrolyzer	:	Multi-Shot Pyrolyzer (EGA/PY-3030D, Frontier Laboratories)
GC/MS	:	Quadrupole GC/MS of Agilent, Shimadzu, etc.
Separation column	:	Ultra ALLOY-5 (5% diphenyldimethylpolysiloxane) L=30 m, id=0.25 mm, df= 0.25 µm (MS/HT) (P/N : UA5 (MS/HT)-30M-0.25F, Frontier Laboratories)

B. Sample and sample cup

Weight of sample	:	approx. 0.1 mg
Sample shape	:	Powder (Polymer Prepper used, details in section CHAPTER6)
Sample cup	:	Disposable Eco-Cup LF (80 µL, P/N : PY1-EC80F)
Sampler	:	Double-Shot or Single-Shot sampler or alternatively Auto-Shot sampler may be used.

C. Temperature and gas flow rate

PY

Pyrolyzer	:	400ºC
PY-GC ITF temp.	:	300ºC

GC

GC oven temp.	:	40ºC (2 min) - 320ºC (20ºC/min, 14min hold)
GC injector temp.	:	300ºC
GC/MS ITF temp.	:	280ºC
Carrier gas	:	Helium
Split ratio	:	1/100
Column flow rate	:	1 ml/min

MS

Mass range	:	m/z 29 - 550
Sampling rate	:	2 (3 scans/sec)
Threshold level	:	200 counts
Multiplier	:	200 V below the voltage set by Autotune

CHAPTER 9 Py-GC/MS ANALYSIS FOR ADDITIVES

9.1 Py-GC/MS technique and its flow configuration

Based on experiences accumulated over years of extensive research efforts, the additive library has been developed from mass spectral data obtained using flash pyrolysis GC/MS (Py-GC/MS) and also thermal desorption GC/MS (TD-GC/MS) for some additives. Since the concentration of the additives in various polymer formulations is generally on the order of 0.1%, peak intensities in pyrograms are significantly smaller than those of the pyrolyzates; therefore, pretreatments such as solvent extraction, column chromatography, etc. are usually required. After the pretreatment, analysis of the additives is performed using Py-GC/MS. If a multi-shot pyrolyzer is used, the pretreatment can be simplified by using thermal desorption or heart-cut techniques using Selective Sampler.

The general construction of a Py-GC/MS system is illustrated in Fig. 9.9-1. In section 9.2, the analytical conditions used for the library are described in detail. The sample cup is dropped (free-fall) into the center of the pyrolysis furnace which is at 600ºC and the sample is instantly pyrolyzed. Pyrolyzates pass through the split/splitless injection port of the GC and ca. 1/100 of them reach the separation column. The pyrolyzates are separated by GC and detected by a mass spectrometer (MS). Using the Selective Sampler, only target additives can be analyzed by heating the furnace to the elution temperatures of the additives.

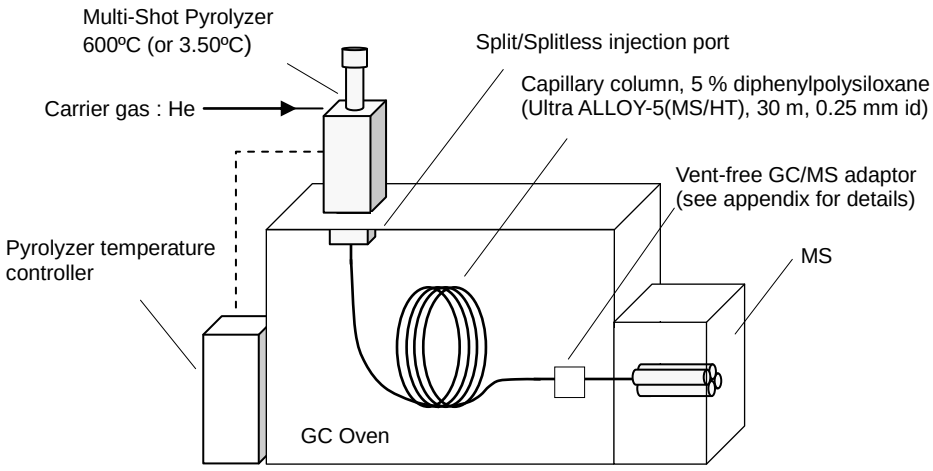


Fig. 9.9-1 Flow configuration in Py-GC/MS analysis

9.2 Analytical conditions for ADD-MS library

The analytical conditions under which the ADD-MS library data were obtained are shown in Fig. 9.9-1　Flow configuration in Py-GC/MS analysisThese are the same as those used for the data acquisition of the PyGC-MS library.

The construction of this library is identical to that used for conventional libraries such as NIST and Wiley. It is a compilation of mass spectra of the various components of the additive. A mass spectrum from a peak on the TIC chromatogram is searched against the additive library (ADD-MS library) and candidate compounds are displayed in the order of match quality. As in the case for pyrograms, the mass spectra as well as the chromatograms can be compared side by side. Retention indices (RI)[*1] are also included in the displayed list. The mass spectra of the unknown and the library entry must be similar and the RI value must be similar in order to narrow down the candidate compounds.

[*1] : The retention index (RI) is based on an index calculated by multiplying the number of a saturated hydrocarbon by 100, and is not much influenced by the type of GC separation column or oven temperature.

9.2.1 Analytical conditions for Py-GC/MS and TD-GC/MS

A. Instruments

Pyrolyzer	: Multi-Shot Pyrolyzer (EGA/PY-3030D, Frontier Laboratories)
GC/MS	: Agilent 5973, JEOL JMS-AM SUN, Shimadzu QP2010
Column	: Ultra ALLOY-5 (5 % diphenyldimethylpolysiloxane) L=30 M, id=0.25 mm, 0.25 µm film thickness (MS/HT) (P/N: UA5(MS/HT)-30M-0.25F, Frontier Laboratories)

B. Sample and sample cup

Amount of sample	: ca. 0.03 mg
Sample form	: Powder or liquid
Sample cup	: Disposable Eco-Cup LF (80 µl, P/N: PY1-EC80F)
Sampler	: Auto-Shot sampler (P/N: AS-1020E) or Manual sampler

C. Temperature and flow conditions

PY

PY temperature	: 600 ºC
TD temperature	: 400 ºC
(antioxidant)	: 340 ºC
PY/GC ITF temp.	: 300 ºC

GC

Oven temperature	: 40 ºC(3 min hold) – 20 ºC/min – 320 ºC(14 min hold)
Injection port temp.	: 300 ºC
GC/MS ITF temp.	: 280 ºC
Carrier gas	: Helium
Split ratio	: 1/100
Column flow rate	: 1 mL/min

MS

Mass range	: m/z 29 - 1,000
Sampling rate	: 2 (3 scan/sec)
Threshold level	: 200 counts
Multiplier	: 200 V below the voltage set by Autotune

9.2.2 Notes on collecting thermal desorption or pyrolysis data for additives

About samples

A. Analyzing samples that contain additives at high concentrations.

These samples have extremely high concentrations of target analytes, therefore, TIC chromatograms will be very similar to those found in the ADD-MS16B library. The main component in the TIC is a large peak and may saturate the MS detector. This results in a mass spectrum which is often quite different from the expected or typical spectrum for that compound. This has a adverse effect on the search results. To judge whether a peak is saturated or not, move the cursor to the rise or down point of the peak where the intensity is low, and compare the mass spectra.

B. Analyzing samples that contain less than 0.1% of additives.

B1) Normal pretreatment: these samples have extremely low concentrations of target analytes; peaks may be unresolved or undetected. If this is the case, purify and concentrate the target compounds using techniques such as solvent extraction, column chromatography, etc. After the pretreatment, use Py-GC/MS and focus on the pyrolyzates of the additives of interest which can be identified using the additives library. Quantitation can be performed using mass chromatograms of the characteristic ions. To accomplish this, select [View] – [Mass Chromatogram] from the F-Search menu.

B 2) Simple pretreatment using a Multi-Shot Pyrolyzer: this eliminates most sample pretreatment. The method involves performing evolved gas analysis (EGA) to determine the elution temperature range of the target additive. This is followed by a thermal

desorption analysis over the temperature range determined. If the target compound has less than 20 carbons, a cold-trap at the head of column is required. If the sample is a powder, then place the sample in the sample cup (L), and plug it with a bit of clean quartz wool. This prevents the sample from contaminating the pyrolyzer.

For other precautions, see CHAPTER 7 of this manual.

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