C146-E384

SHIMADZU
Excellence in Science

Technical Report

Detailed Analysis of an Unknown Polymer Using the Py-GC/MS System with Polymer Additives and F-Search Polymer Libraries

Yukihiko Kudo[1], Kazuhiro Kawamura[1], Koki Tanaka[1], Atsushi Watanabe[2], Kazuko Matsui[2], and Chuichi Watanabe[2]

Abstract:

The analysis of additives contained in polymer materials is important for managing and improving the quality of these materials, and for complying with regulations on chemical substances. The Polymer Additives Library is a GC/MS mass spectra library containing information on a wide range of additives used in polymer materials. Along with mass spectra, the library contains information on retention indices, additive classification, and decomposition products that allow detailed analysis of additives.
This report describes analysis of an unknown polymer using three analysis modes on a Py-GC/MS system (evolved gas MS, pyrolysis GC/MS, and thermal extraction GC/MS), and estimation of the polymer base material and additives contained in the polymer using the Polymer Additives Library and Frontier Laboratories' F-Search Polymer Library. The polymer base material was estimated to be Styrene-butadiene rubber (SBR), containing the antioxidant additive p-(p-Toluene sulfonylamido)diphenylamine (Nocrac TD).

Keywords: Py-GC/MS, polymer, additive, Polymer Additives Library, F-Search

1. Introduction

The analysis of trace additives in polymer materials is becoming increasingly important for the quality control and research and development of polymer materials, and for compliance with increasingly stringent regulations on chemical substances. Currently, a method widely used for analysis of trace additives in polymer materials is to combine GC/MS, which has excellent selectivity and can detect different additives with high sensitivity at several tens to several hundred ppm, with an existing NIST or Willey general-purpose mass spectra library.[1)] A drawback of this method is that general-purpose libraries contain only a limited number of additives commonly used in polymer materials, so some additives escape detection. Some additives also undergo pyrolysis or modification during heating or mixing operations after addition, and though these altered chemical forms can be identified by searching a general-purpose library, identifying the original target additive, which is the original purpose, is more difficult, and many years of experience and knowledge are required to infer the original additive based on its pyrolysates.

Therefore, to allow efficient analysis of additives in polymer materials, we developed a new GC/MS mass spectra library, the "Polymer Additives Library," specifically for additives used in polymer materials.

We used this library to perform qualitative analysis of antioxidants and other additives present in a polymer of unknown formulation, and to verify the utility of the library. Detailed analysis of the polymer was also performed using the F-Search Polymer Library[2)], which enables compositional analysis of polymers based on results obtained from evolved gas MS analysis and pyrolysis GC/MS analysis.

1 Shimadzu Corporation
2 Frontier Laboratories Ltd.

1-1. Overview of Polymer Additives Library

- **Number of spectra: 4,869 (Includes additives and additive pyrolysates)**

  In addition to the existing ADD-MS16B F-Search Additives Library (Frontier Laboratories), a library developed exclusively by Shimadzu has been added that contains mass spectral data for an additional 65 compounds often targeted for analysis, selected based on their usage in the commercial market, and chemical regulatory information (REACH, GS Mark, etc.).

- **Inclusion of Retention Indices Information**

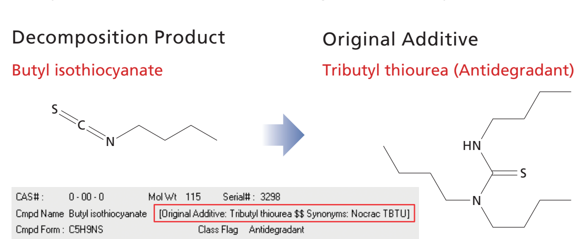
  Results with a high degree of similarity can be obtained by using retention indices to reduce the number of library search results.

- **Inclusion of Information on Additive Classification**

  Even without detailed knowledge of additives, compounds that appear in search results can be identified based on their role as an additive, such as a plasticizing agent or a flame retardant.

- **Original Additive Can Be Estimated Based on Decomposition Products of Additive**

  This library contains information on decomposition products linked to their original additive, and allows estimation of the original additive without the need for years of experience in additive analysis or a broad understanding of chemistry.



2. Experiments

2-1. Instruments

Measurements were taken using the EGA/PY-3030D multi-shot pyrolyzer (Frontier Laboratories), and the GCMS-QP2020 gas chromatograph quadrupole mass spectrometer (Shimadzu). The Polymer Additives Library and the NIST Library (2014 version) were used for qualitative analysis of additives by thermal extraction GC/MS. The F-Search Polymer Library (Frontier Laboratories) was used for qualitative analysis of polymer base material by evolved gas MS analysis and pyrolysis GC/MS analysis. Detailed analytical conditions are shown in Table 1.

2-2. Sample Preparation

A sheet of vulcanized rubber (thickness: 2 mm) of unknown base material and unknown additive formulation was used as the sample. Pieces were cut from this sheet using a micro-punch of 0.5 mm internal diameter. Approximately. 0.5 mg of these pieces were placed in an inert sample cup for use in pyrolysis and weighed, then used as the analytical sample.

2-3. Analysis

(1) Evaluation of thermal characterization and estimation of polymer composition by evolved gas MS analysis

Samples were analyzed by the evolved gas MS method, and we evaluated the temperature regions in which volatile components and polymer pyrolysates were detected. The mass spectra of polymer pyrolysates were then analyzed using the EGA-MS F-Search Polymer Library Ver. 3.5 (Frontier Laboratories), and qualitative analysis was performed on the polymer base material.

(2) Analysis of polymer composition by pyrolysis GC/MS analysis

Samples were analyzed using the pyrolysis GC/MS method, the resulting pyrogram mass spectra were analyzed using the Py GC-MS F-Search Polymer Library Ver. 3.5 (Frontier Laboratories), and qualitative analysis was performed on the polymer base material.

(3) Analysis of additives by thermal extraction GC/MS

Volatile components obtained in analysis (1) were subjected to thermal extraction GC/MS analysis in the temperature regions in which those volatile components were detected, and qualitative analysis was performed on each detected peak using the Polymer Additives Library (Shimadzu) and the NIST Library (2014 version).

Table 1 Analytical Conditions

Instruments	
Py	: EGA/PY-3030D multi-shot pyrolyzer (Frontier Laboratories)
GC-MS	: GCMS-QP2020 (Shimadzu)
Evolved Gas MS Method	
[Py]	
Analysis Mode	: Evolved gas
Pyrolysis Temperature	: 100°C - 20°C/min - 700°C
ITF Temperature	: 320°C (Auto)
[GC-MS]	
Column	: Ultra Alloy EGA tube (2.5 m x 0.15 mm I.D.)
Oven Temperature	: 300°C
Sample Injection Unit	: 320°C
Carrier Gas	: He (1 mL/min)
Injection Method	: Split (1:50)
ITF Temperature	: 280°C
Ion Source Temperature	: 230°C
Measurement Mode	: Scan (*m/z*: 29 – 600)

Pyrolysis GC/MS Method	
[Py]	
Analysis Mode	: Single shot
Pyrolysis Temperature	: 600°C
ITF Temperature	: 320°C (Auto)
[GC-MS]	
Column	: UA-5MS/HT (30 m x 0.25 mm I.D., df=0.25 µm)
Oven Temperature	: 40°C (2 min) - 20°C/min - 320°C (14 min)
Sample Injection Unit	: 320°C
Carrier Gas	: He (linear velocity = 36.1 cm/sec)
Injection Method	: Split (1:100)
ITF Temperature	: 280°C
Ion Source Temperature	: 230°C
Measurement Mode	: Scan (*m/z*: 29 – 600)
Thermal Extraction GC/MS Method	
[Py]	
Analysis Mode	: Heart-cut EGA (thermal extraction method)
Pyrolysis Temperature	: 100°C - 20°C/min - 340°C (1 min)
ITF Temperature	: 300°C (Auto)
[GC-MS]	
Column	: UA-5MS/HT (30 m x 0.25 mm I.D., df=0.25 µm)
Oven Temperature	: 40°C (2 min) - 20°C/min - 320°C (16 min)
Sample Injection Unit	: 300°C
Carrier Gas	: He (linear velocity = 36.1 cm/sec)
Injection Method	: Split (1:100)
ITF Temperature	: 280°C
Ion Source Temperature	: 230°C
Measurement Mode	: Scan (*m/z*: 29 – 800)

3. Results and Discussion

3-1. Compositional Analysis of Polymer Base Material by Evolved Gas MS Analysis

A thermogram obtained from the sample by evolved gas MS analysis is shown in Fig. 1. Additives and other volatile components were detected between 100 °C and around 340 °C, and a polymer-derived pyrolysate was detected at higher temperatures. The mass spectrum of this pyrolysate was used to search the F-Search EGA-MS Polymer Library, revealing 97 % spectral similarity with Styrene-butadiene rubber (SBR). The sample thermogram obtained was also confirmed to be similar to the pyrogram pattern for SBR. Based on these results, the polymer base material was estimated to be SBR (Fig. 2).

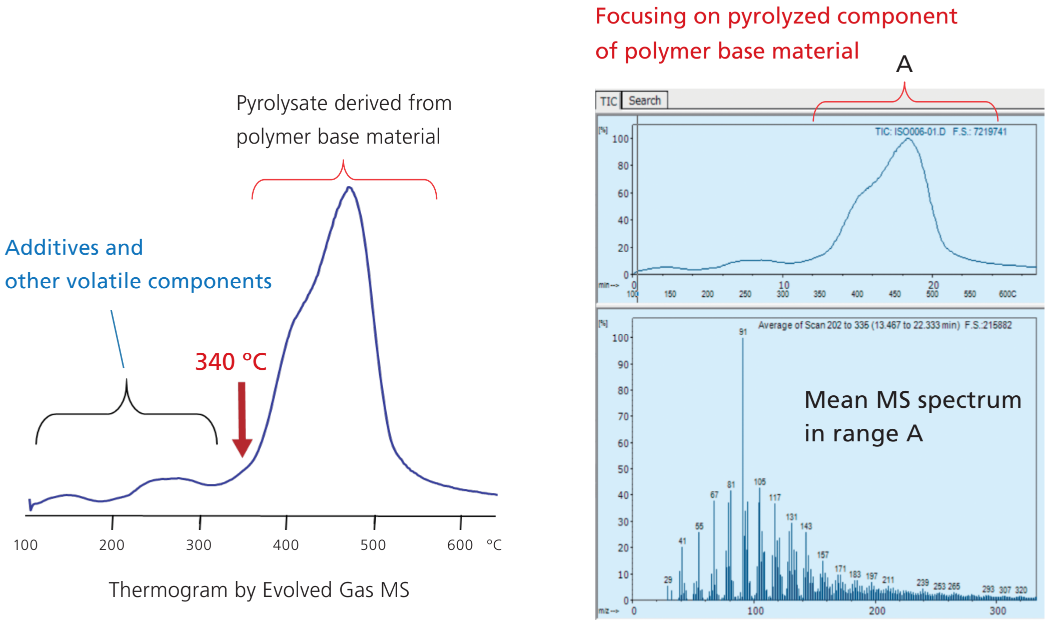


Fig. 1 Thermogram Obtained by Evolved Gas MS Analysis and MS Spectrum of Pyrolyzed Component of Polymer Base Material

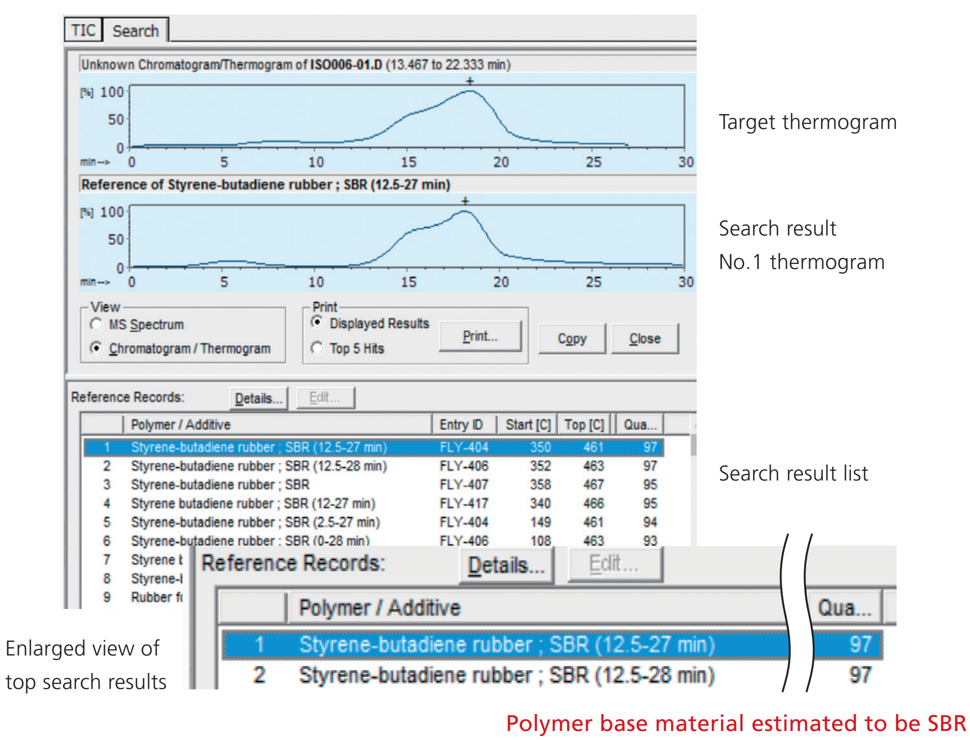


Fig. 2 Results from Compositional Analysis of Polymer Base Material Using Evolved GC/MS F-Search Polymer Library

3-2. Compositional Analysis of Polymer Base Material by Pyrolysis GC/MS Analysis

Next, a mass spectrum of the group of peaks detected in the pyrogram obtained by pyrolysis GC/MS analysis was analyzed using the F-Search Polymer Library (Fig. 3). This analysis revealed a similar result to that described in section 3-1, of 96 % spectral similarity with SBR. The sample pyrogram obtained was also confirmed to be similar to the pyrogram pattern for SBR. Based on the results of 3-1 and 3-2, the polymer base material was estimated to be SBR.

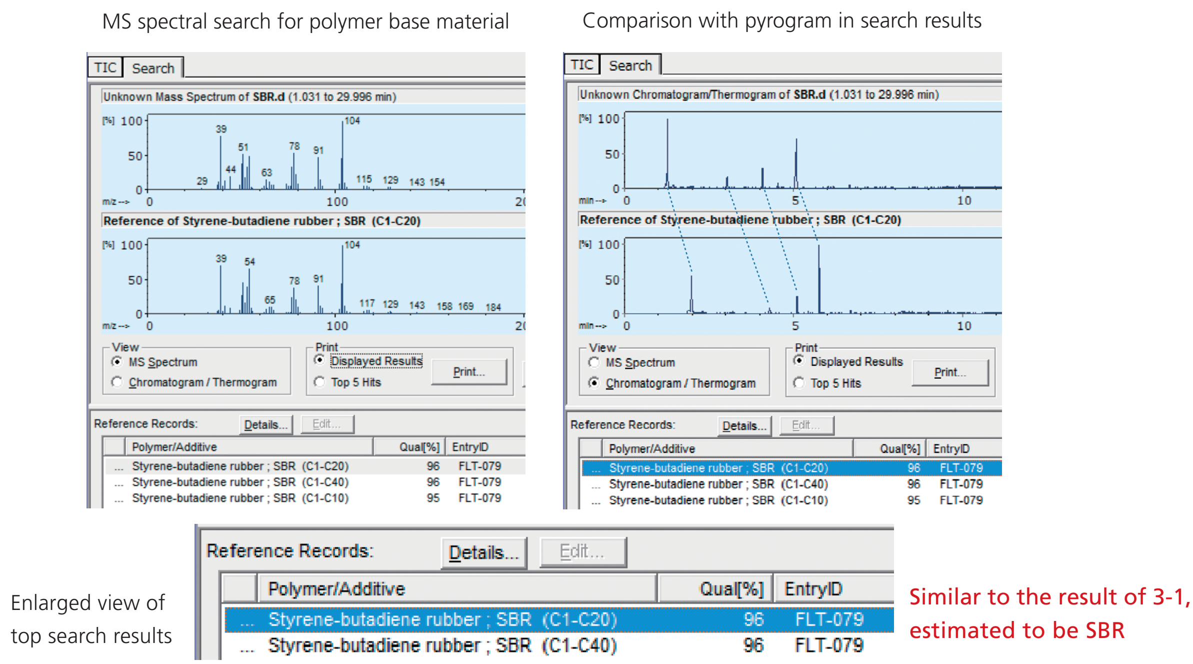


Fig. 3 Results from Compositional Analysis of Polymer Base Material Using Pyrolysis GC/MS F-Search Polymer Library

3-3. Qualitative Analysis of Additives by Thermal Extraction GC/MS Analysis

Based on the information in the thermogram obtained in section 3-1 by evolved gas MS analysis, we performed thermal extraction GC/MS analysis in the temperature range that extracted volatile components (100–340 °C), then qualitative analysis was performed on the major peaks using the NIST Library and the Polymer Additives Library (Fig. 4).

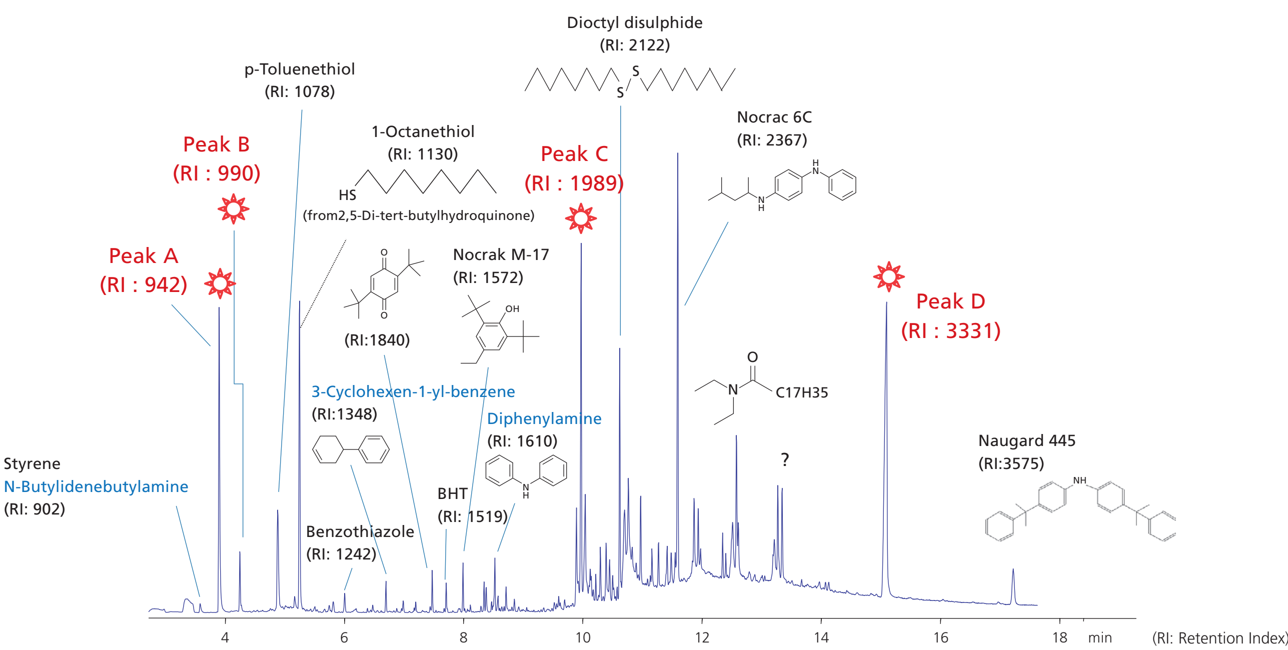


Fig. 4 Total Ion Current Chromatogram Obtained by Thermal Extraction GC/MS Analysis, and Results from Qualitative Analysis of Each Detected Peak

Use of the cross-linking agent Irgacure, and use of the antioxidants BHT, Nocrac M-17, Nocrac 6C, and Nocrac CD, were estimated based on search results obtained from both the NIST Library and the Polymer Additives Library. For peaks A through D, compounds identified with the NIST Library had only a low degree of similarity, which did not provide clear results. Furthermore, though the pyrolysates on the pyrogram could be estimated using the NIST Library, we were unable to estimate the original additives before their pyrolysis. Meanwhile, for these peaks, the Polymer Additives Library allowed us to estimate the compound together with information on similarity, retention indices, and other parameters (Fig. 5).

Peaks A and B were estimated to be Dibutyl amine and Butyl isocyanate, and based on original information on additives included in the Polymer Additives Library, we also estimated these compounds were derived from Tributylthiourea, an antioxidant. Peak C was estimated to be N-Phenyl-1,4-benzenediamine, and based on original information on additives, was estimated to be a pyrolysate, generated during compound forming, of Peak D. Peak D was estimated to be p-(p-Toluene sulfonylamido)diphenylamine (Nocrac TD), an antioxidant additive.

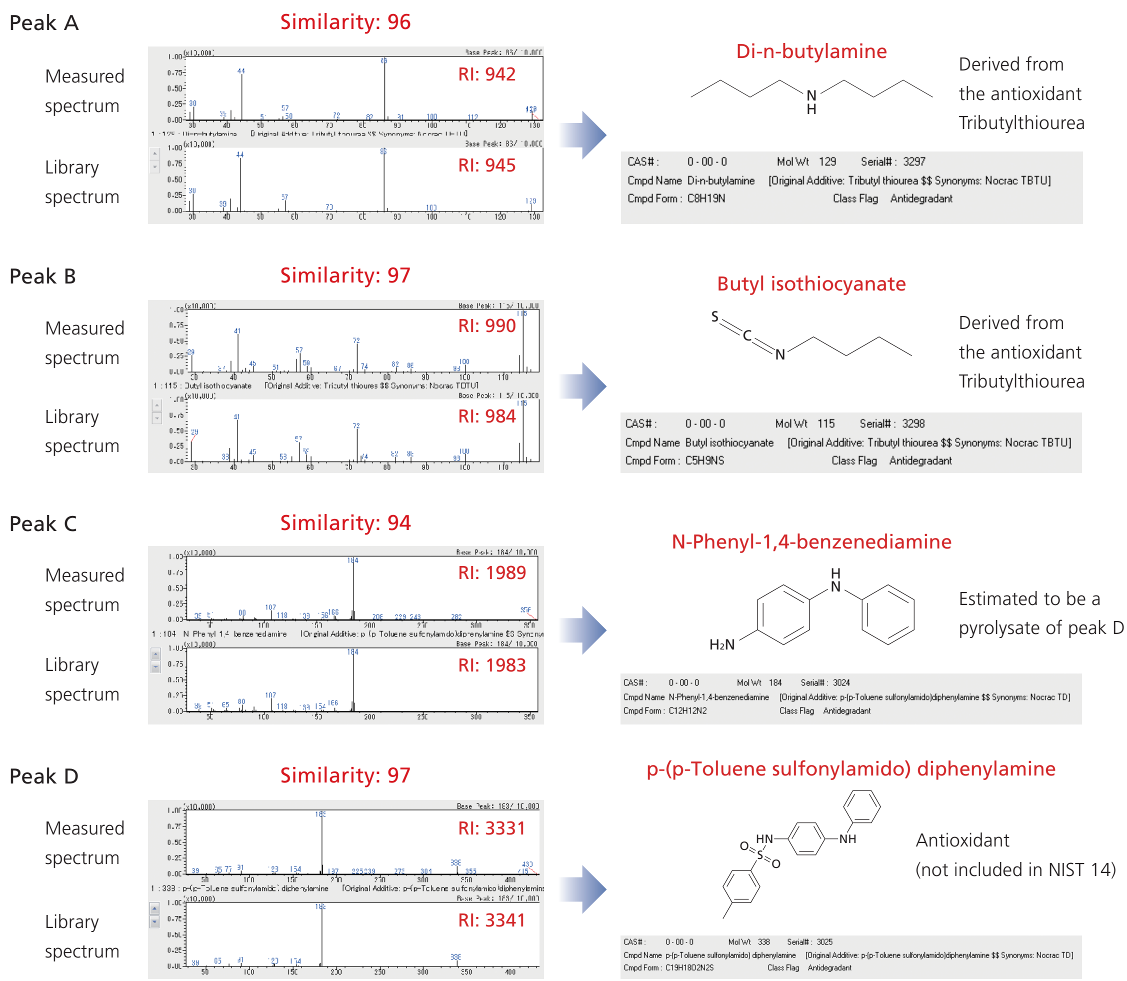


Fig. 5 Results from Qualitative Analysis of Peaks A, B, C, and D Using the Polymer Additives Library

4. Conclusion

The Polymer Additives Library allowed us to estimate additives based on peaks that we had difficulty identifying using a general-purpose library. The Polymer Additives Library also allowed us to easily estimate the original additive from its detected pyrolysates, a task that typically requires extensive experience and knowledge. We were also able to estimate the base material of an unknown polymer using the F-Search Polymer Library. This showed that an unknown polymer sample can be analyzed in detail using a combination of the Polymer Additives Library and the F-Search Polymer Library.

References

1) K. D. Jansson, C. P. Zawodny, T. P. Wampler, *J. Anal. Appl. Pyrolysis,* 79 (2007) 353-361
2) A. Hosaka, K. Ito, I. Watanabe, C. Watanabe, Shimadzu GC/MS Technical Report No. 9

GC/MS Mass Spectra Library

Polymer Additives Library

The Polymer Additives Library is a GC/MS mass spectra library containing information on a wide range of additives used in polymer materials. In addition to approx. 4,900 mass spectra, the library contains information on retention indices, additive classification, and decomposition products that enable easy analysis of additives without the need for an extensive understanding of additives. The library can be used with pyrolysis GC/MS and a variety of other GC/MS systems, including liquid sample injection GC/MS.

Filtering with Retention Index

Multiple compounds with similar mass spectra are listed as candidates when performing a library search using only the mass spectrum. Filtering with the retention index sorts the candidates by retention index, thereby providing highly accurate identification results.

Results of similarity search using a mass spectrum

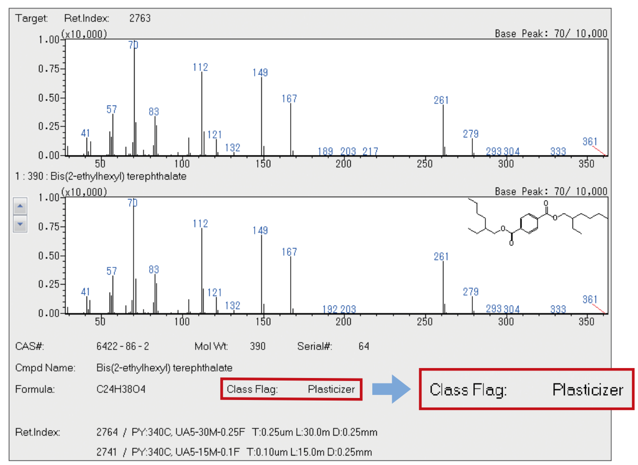
Hit#	Similarity	Register	Ret. Index	Compound Name	Mol Wt	Formula	Library
1	95	☑	1729	Ethylhexyl benzoate [Original Additive: Bi	234	C15H22O2	FLAB_ADD1
2	81	☐	2042	Undecyl benzoate [Original Additive: Diu	276	C18H28O2	FLAB_ADD1
3	81	☐	1796	Octyl benzoate [Original Additive: Tri-n-	234	C15H22O2	FLAB_ADD1
4	79	☐	2109	Tridecyl benzoate [Original Additive: Diun	304	C20H32O2	FLAB_ADD1
5	66	☐	793	1-Octene [Original Additive: Alkyl phosp	112	C8H16	FLAB_ADD1
6	65	☐	791	Isomer of C8H16 [Original Additive: Alkyl	112	C8H16	FLAB_ADD1

Results sorted using retention index filtering

Hit#	Similarity	Register	Ret. Index	Compound Name	Mol Wt	Formula	Library
1	95	☑	1729	Ethylhexyl benzoate [Original Additive: Bi	234	C15H22O2	FLAB_ADD1

Confirming the Additive Classification Information

The additive classification information (such as plasticizers and flame retardants) registered in the library plays a role in confirming the type of additive associated with the compounds included in search results.

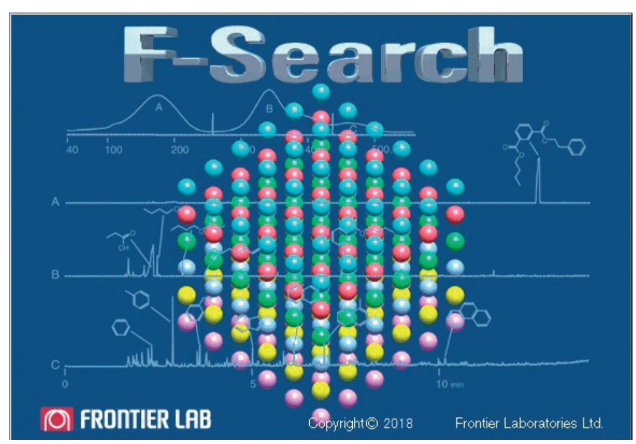


Frontier Laboratories

F-Search Library Ver. 3.6

The F-Search Library Ver. 3.6 is comprised of the F-Search software and different polymer libraries, and enables high-speed searching for polymers and additives based on EGA thermograms and pyrograms. Ver. 3.6 comes with an increased number of polymers in three polymer libraries.

1) EGA-MS Polymer Library: 1,000 in total
(300 polymers added)
2) PyGC-MS Polymer Library: 1,000 in total
(300 polymers added)
3) Pyrolyzate-MS Polymer Library: 268 in total
(103 polymers added)
4) ADD-MS Additives Library: 494 in total



First Edition: June, 2019

SHIMADZU

Shimadzu Corporation
www.shimadzu.com/an/

Printed in Japan 3655-02904-15AIT