

Rubber and Plastic Materials Characterization Using Micro-Furnace Multi-Mode Pyrolysis-GC/MS



Why Pyrolysis-GC/MS?

Manufacturers are always seeking new technologies and developments that increase production efficiency and the quality of the produced parts. Many analytical protocols used to analyze rubber and plastic components require multi-step sample preparation prior to chromatographic analysis.

These procedures often include solvent extraction, filtration, and concentration. These traditional techniques are cumbersome, time-consuming, and suffer from analyst-to-analyst variability while producing data of limited value.

Samples are analyzed “as is” when using the Frontier Micro-Furnace Pyrolyzer. No sample preparation is needed. Eliminating the solvent extraction process enhances the precision of quantitative analysis while virtually prevent sample contamination and improves analytical efficiency. These are three of the primary reasons many manufacturing and polymer development laboratories utilize the Frontier Pyrolyzer.

The Multi-Shot Micro-Furnace Pyrolyzer can be configured in a number of different ways, so that a sample can be characterized using various analytical techniques, including evolved gas analysis, thermal desorption, flash pyrolysis, double-shot, Heart-Cutting of individual EGA thermal zones, and reactive pyrolysis.

Initially, such diversity may be perceived as a complicated decision process: what analytical mode will give us the most insight into the nature of the sample in the least amount of time? To assist, Frontier scientists have created a “method map” for material characterization. An overview of the “method map” is provided on [page 44](#).



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A-1

Determination of Antioxidants in NBR Rubber

❖ **PROBLEM:** What is the best method to quantitate additives in rubber?

❖ **SOLUTION:** A piece of an acrylonitrile-butadiene rubber sample (NBR) weighing about 1 mg is placed in an inert sample cup. Using the micro-furnace multi-mode pyrolyzer directly interfaced to a GC/MS system, the sample was analyzed. EGA and thermal desorption-GC/MS modes of operations were used.

❖ **RESULT:** The EGA thermogram of the NBR sample, containing various types of additives, is shown in Fig. 1. This suggests that the volatile components are desorbed in zone A. Fig. 2 shows the (TD)-GC/MS chromatogram of zone A fraction. Table 1 shows the results that the reproducibility of the relative peak intensities for two types of antioxidants is less than 2% RSD.

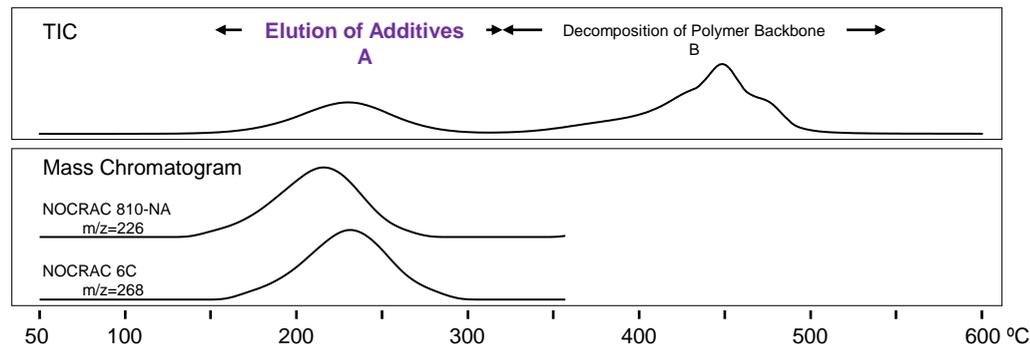


Fig. 1. Evolved Gas Analysis of NBR

Table 1. Reproducibility of Area Ratios (vs ISTD) of NBR additives

n	NOCRAC 810-NA	NOCRAC 6C
1	0.113	0.139
2	0.118	0.140
3	0.119	0.144
4	0.122	0.143
5	0.124	0.140
6	0.123	0.144
7	0.123	0.144
8	0.124	0.143
Aver.	0.122	0.143
RSD	1.98 %	1.27 %

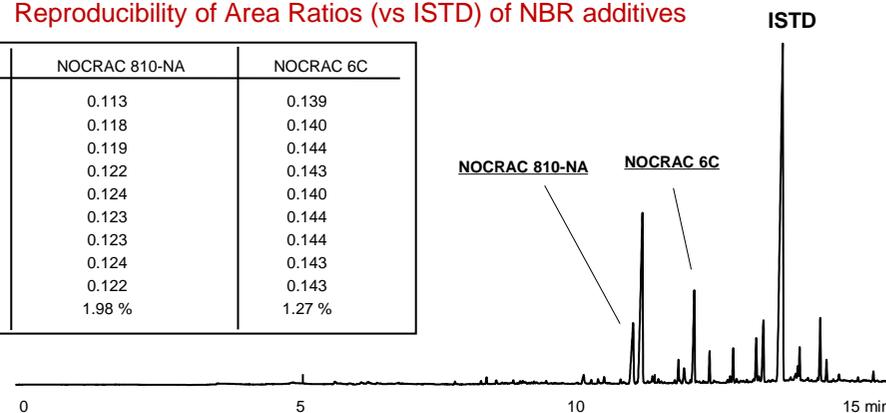


Fig. 2 Chromatogram for Zone A by (TD)-GC/MS analysis

NOCRAC810-NA: N-Phenyl-N'-isopropyl-p-phenylenediamine

NOCRAC 6C: N-Phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine

A-2 Analysis of Compounded Rubber

❖ **PROBLEM:** How can a compounded rubber be analyzed using Multi-Shot pyrolyzer? What information can be obtained?

❖ **SOLUTION:** A compounded rubber is analyzed by Multi-Shot pyrolyzer operating in double-shot mode, Thermal Desorption (TD), followed by flash pyrolysis (PY). Following the “Method Map” methodology, Evolved Gas Analysis (EGA) was first performed to obtain the sample’s thermal profile.

❖ **RESULT:** Fig. 1 shows an EGA thermogram of a compounded rubber. Weak peaks are observed in 100~300 °C zone due to the thermal desorption of additives. In 300~500 °C zone, a broad peak due to thermal decomposition of the rubber is observed. From this result, thermal desorption was performed from 100 to 300 °C (20 °C/min), and then flash pyrolysis was done at 550 °C. Fig. 2 shows results of analysis. In the chromatogram of thermal desorption shown in Fig. 2a, cyclic siloxanes (D3~D6) originated from silicon coupling agent, benzothiazole (vulcanization accelerator), higher aliphatic acid (vulcanizing agent), and waxes (antioxidants) were observed. Because isoprene and limonene were mainly observed in the pyrogram shown in Fig. 2b, the major component of this sample is natural rubber.

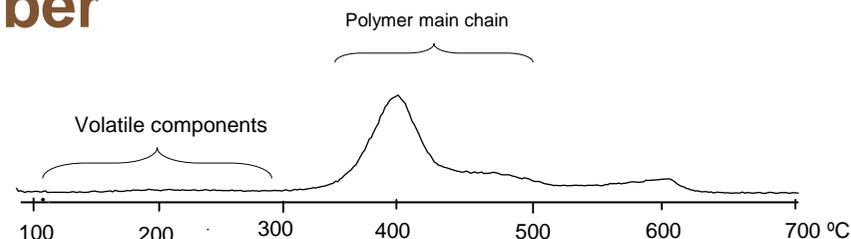


Fig. 1 Evolved Gas Curve of a Compounded Rubber

Pyrolysis temp.: 100 - 700 °C (20 °C/min), Carrier gas : He 50 kPa, Split ratio : ca. 1/20
EGA capillary tube : 0.15 mm id, 2.5 m (UADTM-2.5N), GC oven temp.: 300 °C
Injection temp.: 320 °C, Sample : ca. 5 µg, Detector : MS (m/z 29 - 400)

Fig.2a. Thermal Desorption Chromatogram (100 - 300°C (20 °C/min))

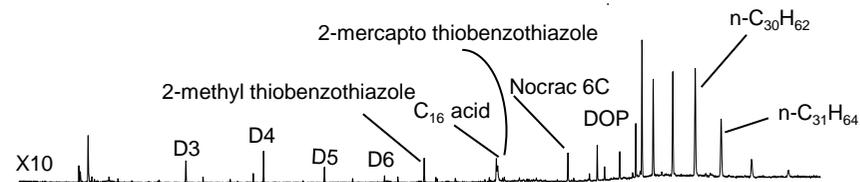


Fig.2b. Pyrogram (550 °C)

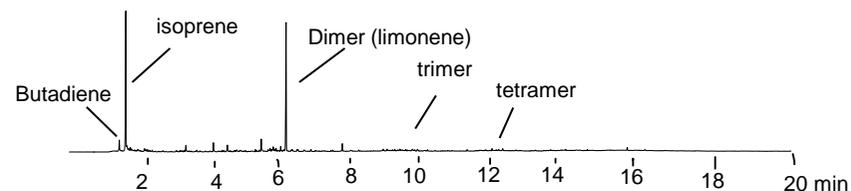


Fig. 2 GC/MS Analysis of Compounded Rubber by Double-Shot Technique

Column flow rate : 1 ml/min (fixed flow rate), Split ratio : 1/20, Separation column: Ultra ALLOY+5 (5% diphenyl polysiloxane), 30 m, 0.25 mm id, Film thickness : 0.25 µm; GC oven temp.: 40 - 300 °C (20 °C/min), Sample : 5 µg, Detector: MS (m/z 29 - 400, 2 scans/sec)

Compositional Analysis of Isoprene-Butadiene-Styrene Blend Rubber

❖ **PROBLEM:** Is there a simple method to analyze the chemical composition of a blended rubber sample?

❖ **SOLUTION:** About 200 µg of a rubber mixture, composed of polybutadiene(PB)- polyisoprene (PI)- polystyrene (PS), is placed in an inert sample cup and pyrolyzed at 550 °C using the micro-furnace multi-shot pyrolyzer.

❖ **RESULT:** Fig.1 shows the pyrogram for the blend rubber sample. The monomers of each component, which are butadiene, isoprene and styrene, are the main pyrolyzates. The calibration curves between relative peak intensities for the specific peaks and the ratio of PB to total weight of the sample shows a fairly good linear relationship with a correlation coefficient greater than 0.99. The calibration curve for the PB composition in the blended sample is shown in Fig.2. Using this calibration curve, a fairly accurate determination of the component is possible within 3% of accuracy.

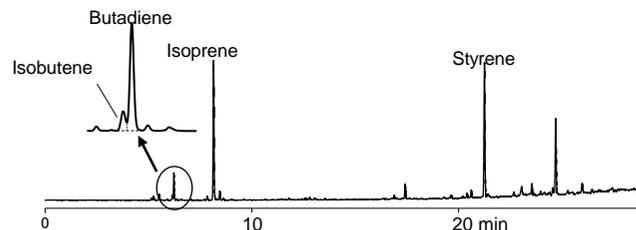


Fig. 1 Pyrogram of standard sample

Pyrolysis temp.: 550 °C, detector: FID, sample: standard sample A
 Separation column: Ultra ALLOY+5 (5% diphenyl 95% dimethylpolysiloxane)
 Length: 60 m, id: 0.25 mm, film thickness: 1.0 µm
 GC oven temp.: 50 °C (7 min hold) – 280 °C (10 °C/min), carrier gas: He
 Injection port pressure: 175 kPa, split ratio: 1/60, sample size: ca.200 µg

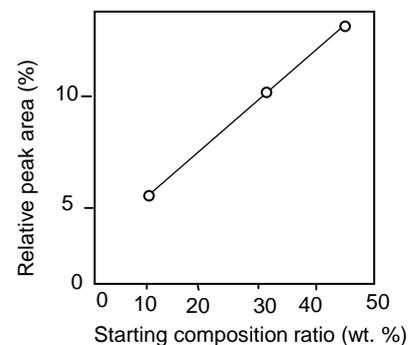


Fig. 2 Calibration curve for PB composition

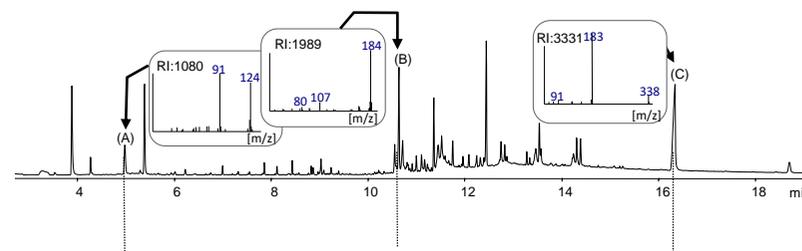
Identification of an Unknown Antidegradant in Rubber

❖ **PROBLEM:** Is there any library search system that allows for the identification of unknown antidegradants used in rubber?

❖ **SOLUTION:** The additive library for F-Search (mass spectra library search engine) contains data for commercially available 32 typical antidegradants. The library consists of mass spectra of major peaks on chromatograms obtained by thermal desorption (TD)-GC/MS method, chemical names, and retention indexes. Analysis of a rubber that contains ca. 1% of unknown antidegradant is described here.

❖ **RESULT:** Fig. 1(a) shows the chromatogram of a rubber sample containing an unknown antidegradant obtained by (TD)-GC/MS and mass spectra for major peaks A, B and C. Major peaks were identified by comparison of mass spectra obtained by library search with their similarity and retention indexes (RI) as shown in Fig. 1(b). Further, from the chromatogram in the library shown in Fig. 1 (b), the antidegradant candidate related to these three compounds was estimated to be p-(p-Toluene sulfonylamido) diphenylamine.

(a) Chromatogram of the volatile components in the unknown rubber sample



(b) Chromatogram of p-(p-Toluene sulfonylamido) diphenylamine in the MS library.

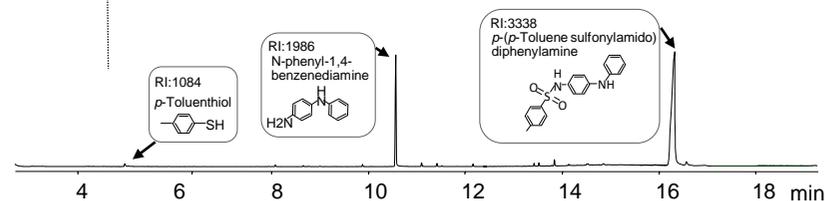


Fig. 1 Chromatograms obtained by TD-GC/MS technique

Furnace temp.: 340 °C (1 min), GC oven temp.: 40 – 320 °C (20 °C/min, 10 min)
Column: Ultra ALLOY-5 (MS/HT) (30 m, 0.25 mm, film thickness 0.25 μm), sample amount: 1.0 mg

Analysis of Rubber Composition with EGA and EGA Polymer MS Library

- ❖ **PROBLEM:** What analytical technique can be used to analyze a rubber of unknown components??
- ❖ **SOLUTION:** The EGA-MS technique is a combination of evolved gas analysis (EGA) and mass spectroscopy (MS) using Multi-Shot Pyrolyzer and is very useful as a primary analytical tool for unknown polymeric samples.
- ❖ **RESULT:** An example on the right is the analysis of a rubber with unknown composition. Shown in Fig. 1 are the EGA thermogram of the rubber and mass spectra of peaks A and B observed. Peak A is considered to arise from additives due to low elution temperatures. To obtain further information, components in peak A need to be analyzed by GC/MS. Peak B is originated from thermal decomposition of the polymer backbone. Table 1 shows the result of library search on the average spectrum of peak B using EGA-MS Library. Polynorbornene and acrylonitrile-butadiene rubber were found as candidate polymers. EGA and library search with EGA-MS Library provide information on the amounts and desorption temperatures of the additives contained in a sample, and is very useful for analysis of unknown materials as a primary technique

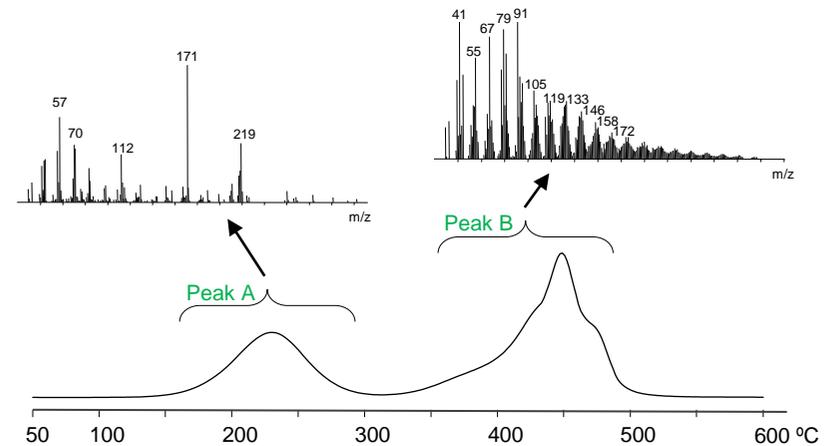


Fig. 1 Evolved Gas Curve of a Rubber and Averaged Mass Spectra
 Pyrolysis temp.:50 - 600 °C (10 °C/min), Carrier gas : He 50 kPa, 60 ml/min, Split ratio :ca.1/50
 EGA capillary tube : 0.15 mm id, 2.5 m (UADTM-2.5N), GC oven temp. : 300 °C
 Injection temp.: 320 °C, Sample :ca. 0.5 mg, Detector : MS, Scan range : m/z 29 - 400,
 Scan speed: 0.1 scans/sec; PY-GC interface temp.: 320 °C (AUTO mode)

Name	Qual
1. Polynorbornene	: 49
2. Polynorbornene	: 43
3. Acrylonitrile-butadiene rubber	: 43

Table 1 Result of Library Search on Peak B

Analysis of Acrylonitrile Butadiene Rubber (NBR) by Double-Shot Technique

- ❖ **PROBLEM:** Because polymeric materials are generally blend of basic polymers and additives, pyrograms obtained by conventional single-shot technique (instant pyrolysis) include both additives and thermal decomposition products of the basic polymer, and this often makes analysis difficult.
- ❖ **SOLUTION:** Double-shot technique is useful because volatile components are thermally desorbed at the first stage, then instant (flash) pyrolysis of the basic polymer follows.
- ❖ **RESULT:** Analysis of NBR is described here as an example. Fig 1 shows a pyrogram of NBR by single-shot method. Thermal decomposition products and additives are shown on a single pyrogram, it is difficult to distinguish the peaks of basic polymer from those of additives. In the double-shot technique (Fig. 2); however, volatiles and additives are eluted off in the first step, whereas thermal decomposition products of basic polymer come off in the second step, allowing much easier identification of peaks. Conditions for thermal desorption and pyrolysis can be determined from EGA curve obtained in evolved gas analysis technique.

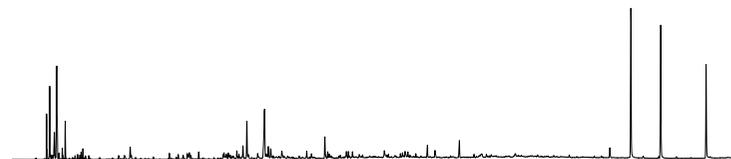


Fig. 1. Pyrogram of NBR by Single-Shot Technique (Total ion chromatogram)

Pyrolysis temp.: 550 °C, Carrier gas : He, Column flow rate : 1.0 ml/min, Carrier total flow rate : 100 mL/min
 Separation column : Ultra ALLOY-5 (5% phenyldimethylpolysiloxane), 30 m, 0.25 mm id, Film thickness : 0.25 µm
 GC oven temp.: 40 °C (3 min) → 10 °C/min → 300 °C (3 min), GC injection port temp.: 320 °C, Sample : 0.31 mg,
 Detector : MS, Scan range : *m/z* 29 - 400

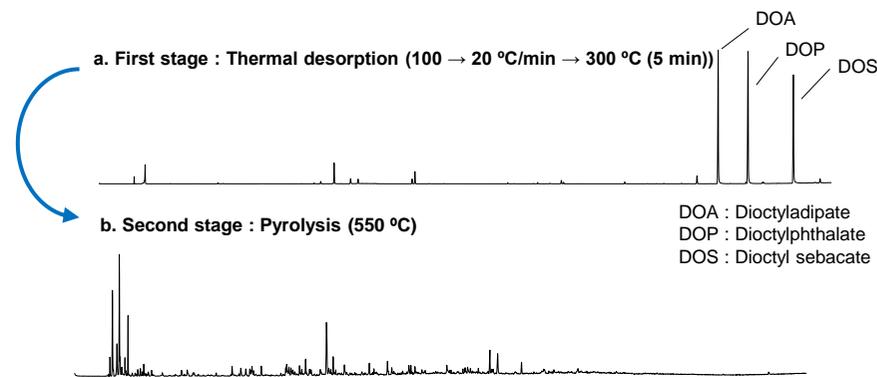


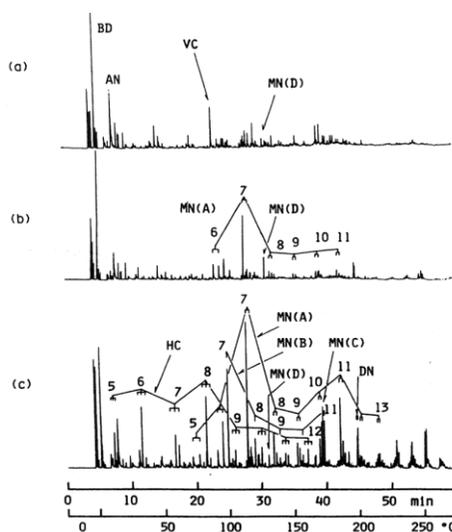
Fig. 2. Pyrogram of NBR by Double-Shot Technique
 Analytical conditions are the same as above (Fig. 1.)

Structural Characterization of Hydrogenated Acrylonitrile-Butadiene Rubbers

❖ **PROBLEM:** Acrylonitrile-butadiene rubbers (NBRs) have relatively low thermal stability due to the presence of double bonds from butadiene (BD). Hence, hydrogenation is required to improve the thermal stability. It is therefore important to characterize their microstructures and hydrogenation mechanism.

❖ **SOLUTION:** Hydrogenated NBRs were prepared by dissolving NBR in THF followed by hydrogenation in the presence of Pd catalyst. About 70 µg each of samples was pyrolyzed at 550 °C under nitrogen carrier gas (50 mL/min). The identifications of peaks were done by a directly coupled GC-MS with both EI and CI sources.

❖ **RESULT:** Figure 1 shows the pyrograms of NBR samples at 550 °C before and after the hydrogenation that were obtained using a fused silica capillary column with poly(dimethylsiloxane) stationary phase. Characteristic peaks in the pyrogram of N-37(0) were butadiene (BD) monomer, BD dimer, and acrylonitrile (AN) monomer; whereas those of hydrogenated NBR consisted of a series of linear mononitriles (MN(A)s) up to C₁₂, each of which consisted of a doublet corresponding to an α-olefinic MN(A) (the former) and a saturated MN(A) (the latter). Another series of mononitrile positional isomers (MN(B)s) are also observed. HC peaks of each carbon number consisted of a triplet corresponding to an α,ω-diolefine, and α-olefin, and a n-alkane.



compound class	abbreviation	sequence
Butadiene	BD	B
Butadiene dimer (4vinylcyclohexane)	VC	BB
Acrylonitrile	AN	A
Hydrocarbons	HC	EE EEE
Mononitriles	MN(A)	EA
	MN(B)	EEA EEEA
	MN(C)	EAE
	MN(D)	BA
Dinitriles	DN	AEA

B = 1,4-butadiene unit; A = acrylonitrile; E = hydrogenated 1,4-butadiene unit

Figure 1. Pyrograms of NBRs before and after hydrogenation at 550 °C separated by a poly(dimethylsiloxane) column: (a) N-37(0); (b) N-37(44); (c) N-37(98). See Table 1 for abbreviations. Numbers indicate carbon numbers of compounds.

Effects of Separation Conditions for Analysis Accuracy in Composition Analysis of A Blend Rubber

- ❖ **PROBLEM:** The Py-GC technique is a useful analytical tool which offers facile and prompt compositional analysis of various blend polymers. With this technique, however, not only peaks due to constituent monomers, but peaks due to various by-products are also observed on the pyrograms and those peaks often overlap, causing the analytical accuracy to be deteriorated. For example, in analysis of a three-dimensional blend rubber such as polybutadiene(PB) - polyisoprene(PI) - polystyrene(PS), depending on the analytical conditions, peaks for butadiene, the monomer of PB, and isobutene, a pyrolysis by-product may not be well resolved on the pyrogram. Here, in this technical note such effects to the analytical accuracy were studied.
- ❖ **SOLUTION:** In the Py-GC system, the Micro-Furnace Multi-Shot Pyrolyzer directly attached to the split/splitless injection port of a GC was connected to an FID via a capillary separation column. The GC separation conditions used were conditions recommended by ISO 7270 (Condition A) and those used to separate isobutene and butadiene in this study (Condition B). Composition ratios of unknowns are determined using a calibration curve generated from three standard samples of varied composition ratios.
- ❖ **RESULT:** Fig. 1 (next page) shows a pyrogram of the PB-PI-PS blend rubber obtained using Condition A, while Fig. 2 shows a pyrogram obtained using Condition B. On both pyrograms, peaks due to the constituent monomers of butadiene (BD), isoprene (IP), and styrene (ST) are observed as major peaks, however, in the pyrogram obtained with Condition A, peaks for IB and BD were not resolved, so it is difficult to obtain the peak area of each peak by integration using a vertical drop line.



Therefore, in calculation of a triplet corresponding to an α,ω -diolefine, and α -olefin, and a n-alkane of composition ratio, peak area was obtained from two peak areas combined and was used as peak area for BD.

On the other hand, in the pyrogram obtained with Condition B, peaks for IB and BD are marginally resolved, thus the peak area of each was obtained by integration using a vertical drop line.

Table 1 shows starting composition ratios and composition ratios obtained with both conditions. In the results obtained with Condition A, composition ratios were obtained with fairly good accuracy, but with regard to PB, relatively large error of -0.8 wt% are shown.

On the other hand, composition ratios obtained with Condition B gave a good accuracy and even the largest error made was mere +0.2 wt% for PS.

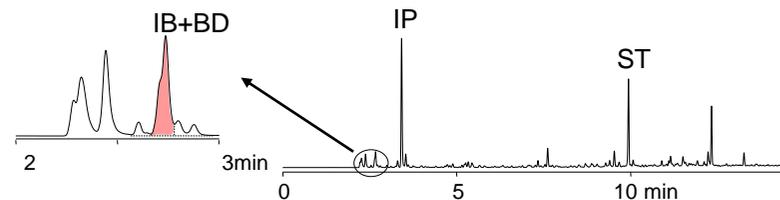


Figure 1. Pyrogram of a blend rubber obtained with conditions recommended by ISO7270 (Condition A)
 Pyrolysis temp. : 550 °C, Detector : FID, Separation column : Ultra ALLOY+-5 (5%-diphenyl-95%-diphenyl-95%-dimethylpolysiloxane); Length 30 m, 0.25 mm id, Film thickness 1.0 μ m; GC oven temp. : 50 °C (2 min hold) – 280 °C (10 °C/min), Injection port pressure : 175 kPa, Split ratio : 1/60, Sample size : ca.200 μ g

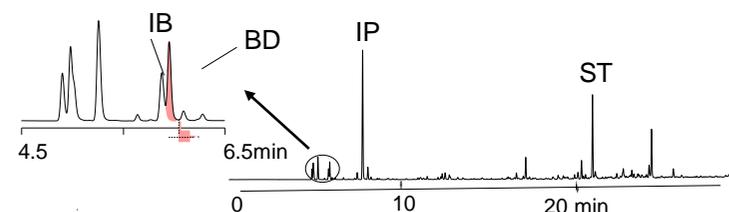


Figure 2. Pyrogram of a blend rubber obtained with conditions used in this study (Condition B)
 Separation column : Ultra ALLOY+-5 (5%-diphenyl-95%-dimethylpolysiloxane), Length 60 m, 0.25 mm id, Film thickness 1.0 μ m; GC oven temp. : 50 °C (7 min hold) – 280 °C (10 °C/min), Other conditions are the same as those in Fig. 1.

	PB	PI	PS
Starting composition ratio	37.2	25.0	37.8
With Condition A	36.4	25.2	38.4
(error)	(-0.8)	(+0.2)	(+0.6)
With Condition B	37.1	24.9	38.0
(error)	(-0.1)	(-0.1)	(+0.2)

Table 1. Composition ratios for unknowns and starting material (wt%)

Determination of Fatty Acids in Vulcanized SBR using Reactive Pyrolysis GC/MS

- ❖ **PROBLEM:** Various additive packages are added to SBR to vary the chemical and physical properties of the polymer. The qualitative and quantitative analysis of these additives generally requires sample pretreatment, such as solvent extraction, to isolate or concentrate the additives of interest.

For example, when analyzing SBR for the total amount of fatty acids, the sample is first extracted using ethanol/toluene followed by titration (ISO 7781 and JIS-K6237); however, this method requires large amounts of solvent, excessive analyst time, and is prone to contamination. The result of this additional 'sample handling' reduces laboratory productivity and results often exhibit poor precision and accuracy.

- ❖ **SOLUTION:** Fatty acids are reactive; the GC peak tails which degrades the accuracy and precision of the peak integration. For this reason, fatty acids are analyzed as methyl esters. Methyl esters are inert, and the GC peaks are symmetrical.

The most efficient method to determine fatty acids in a complex mixture like rubber is reactive-pyrolysis using an organic alkali like tetramethylammonium hydroxide (TMAH).

TMAH hydrolyses the acid and forms the ester at temperatures beyond 250 °C. This technical note demonstrates reactive pyrolysis-GC/MS using TMAH to determine the fatty acids (stearic acid, and palmitic acid) in vulcanized SBR.



❖ **EXPERIMENTAL:** The analysis of the rubber was done using a micro-furnace multi-shot Pyrolyzer (EGA/PY-3030D) directly interfaced to the injector of a GC/MS. The analysis was automated using an Auto-Shot Sampler (AS-1020E). The separation column was an Ultra ALLOY-5 metal capillary column. A Micro Puncher (2 mm) was used to cut a plug of sample (200 µg) which was placed in a sample cup. Next, 2 µL of 25 wt% TMAH was added to the cup and the cup was placed in the Auto-Shot carousel. The sample cup was subsequently dropped into the hot zone (350 °C) of the quartz liner. The derivatized fatty acids were swept through the GC splitter and focused at the separation column inlet.

❖ **RESULT:** The total ion chromatogram of the products formed using reactive pyrolysis have peaks for the methyl esters of palmitic (C16:0) and stearic acid (C18:0) - Fig. 1a. No peak tailing is observed in the extracted ion chromatograms of the M+ ions - Fig.1b and Fig.1c. The concentration of each acid was determined to be 0.16 wt% (C16:0) and 0.46 wt% (C18:0) using the peak area of the M+ ions and a single point external standard calibration. Total fatty acid concentration is 0.62 wt% which is in good agreement with the original formulation concentration of 0.6 wt%. The precision (n=5) of the individual fatty acids determinations is 2.1 and 3.8 % RSD

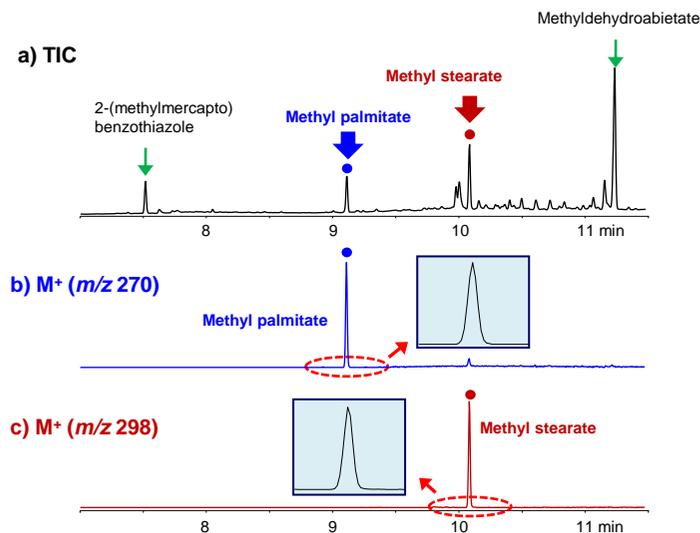


Fig. 1 Chromatogram of vulcanized SBR obtained by reactive pyrolysis-GC/MS

Pyrolysis temp.: 350 °C, GC oven temp.: 70 – 280 °C (20 °C/min, 2 min hold), GC inj temp.: 300 °C
 Separation column: Ultra ALLOY[®]-5 (5% diphenyl 95% dimethylpolysiloxane), L=30 m, i.d.=0.25 mm, df=0.25 µm; Column flow rate: 1 mL/min (He), split ratio: 1/100, sample weight: approx. 200 µg

	Quantitated values (wt%) of fatty acids in vulcanized SBR < formulation concentration 0.6 wt% >		
Sample wt. (µg)	Palmitic acid	Stearic acid	Total fatty acid contents
197	0.160	0.456	0.616
194	0.155	0.441	0.596
203	0.152	0.449	0.601
202	0.156	0.479	0.635
204	0.159	0.479	0.639
Average	0.156	0.461	0.617
RSD (%)	2.12	3.84	3.16

Table 1 Quantitation of total amount of fatty acids in vulcanized SBR and reproducibility (n=5)

Analysis of Brominated Flame Retardant in a Waste Plastics

❖ **PROBLEM:** In the analysis of brominated flame retardants, to be controlled under the Restriction of Hazardous Substances (RoHS directive), GC analysis is generally conducted after solvent extraction, although, it involves cumbersome operations. Therefore, simpler analytical technique needed to be developed. Here, the analysis of decabromodiphenyl ether (DeBDE), a most commonly used brominated flame retardant is achieved by thermal desorption (TD)-GC/MS technique.

❖ **SOLUTION:** A TD-GC system in which a micro-furnace multi-shot pyrolyzer was directly attached to the split/splitless injection port of a GC was used. A polystyrene (PS) based waste plastic containing brominated flame retardants was used as a sample, and an aliquot (5 μL) of THF solution (10 $\mu\text{g}/\mu\text{L}$) was placed in a sample cup for analysis. The temperature of the PY-GC interface and the GC injection port was set to 320 $^{\circ}\text{C}$, at which temperature no absorption or thermal decomposition of DeBDE has been reported. A metal capillary column specifically designed for brominated flame retardants [Ultra ALLOY-PBDE] with highly deactivated inner wall was used.



PLEASE  RECYCLE

❖ **RESULT:** Fig. 1 shows evolved gas analysis (EGA) curves of waste plastic, which was obtained in order to find optimum thermal desorption conditions. The major peak between 400 and 500 °C proved to be derived from thermal decomposition of the base polymer PS. Also a small peak observed between 250 and 350 °C showed m/z 799 and m/z 959 (molecular ion) on the average mass spectrum, hence it was considered to be due to thermally desorbed DeBDE.

From this result, the optimal thermal desorption temperature for DeBDE was determined to be 200–400 °C (20 °C/min). With this thermal desorption condition, the quantitative analysis of DeBDE in the waste plastic was performed by the TD-GC/MS technique.

Fig 2. shows a chromatogram obtained, giving well-resolved peaks without interferences from coexisting species. By this method, it was confirmed that the waste plastic contained 7.1 wt% of DeBDE, with a good reproducibility (RSD=3.5%).

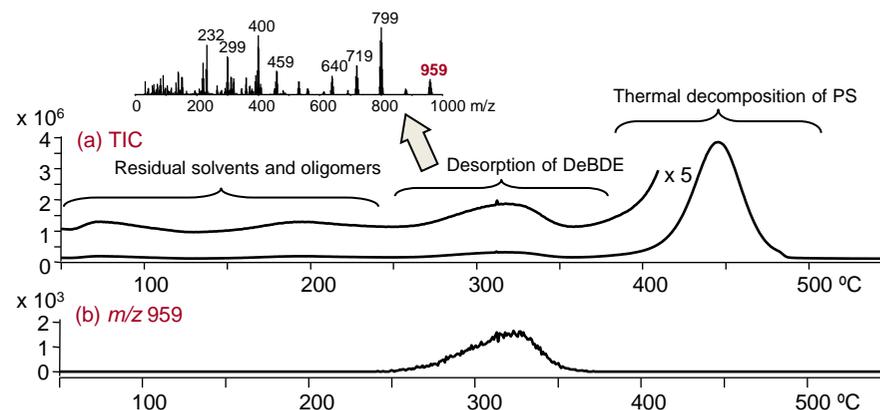


Figure 1 EGA curve of waste plastic

Pyrolysis temp.: 50 - 550 °C (20 °C/min), GC oven temp.: 300 °C, Column flow rate: 1 mL/min, split ratio: 1/50, GC/MS ITF temp.: 320 °C; MS ion source temp.: 250 °C, scan range: 29-1000 (m/z), scan rate: 0.2 scan/sec, sample size: 50 µg

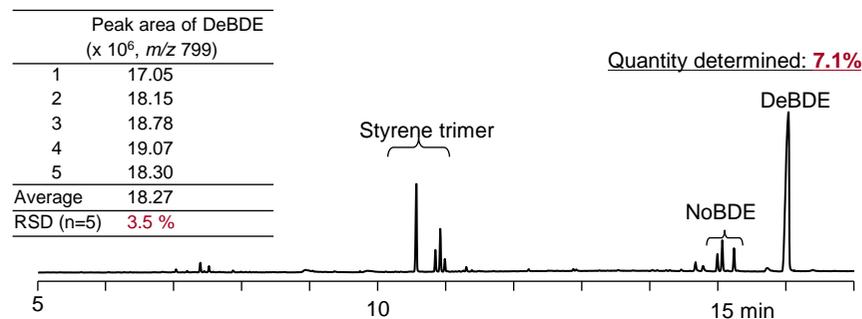


Figure 2 Chromatogram of waste plastic obtained by TD-GC/MS

Pyrolysis temp.: 200 - 400 °C (20 °C/min), Separation column: UA-PBDE (polydimethylsiloxane, length 15 m, 0.25 mm id, film thickness 0.05 µm), Sample size: 50 µg; Column flow rate: 1 mL/min, Split ratio: 1/50, GC/MS ITF temp.: 320 °C, MS ion source temp.: 230 °C, Scan range: 29 - 1000 (m/z), Scan rate: 3 scans/sec

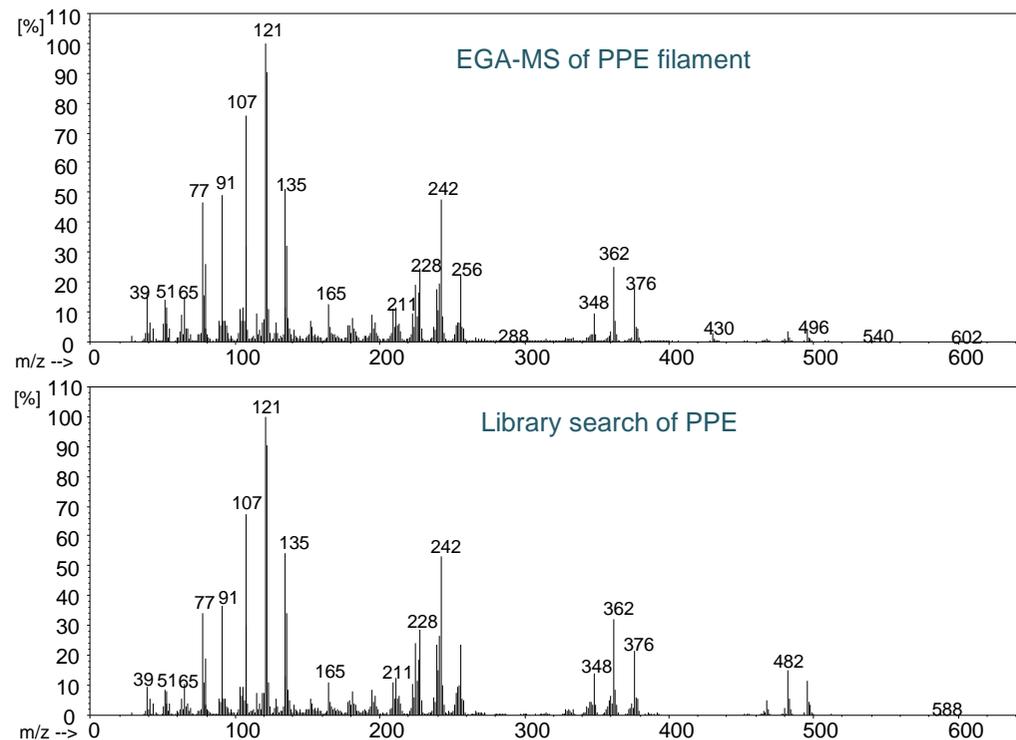
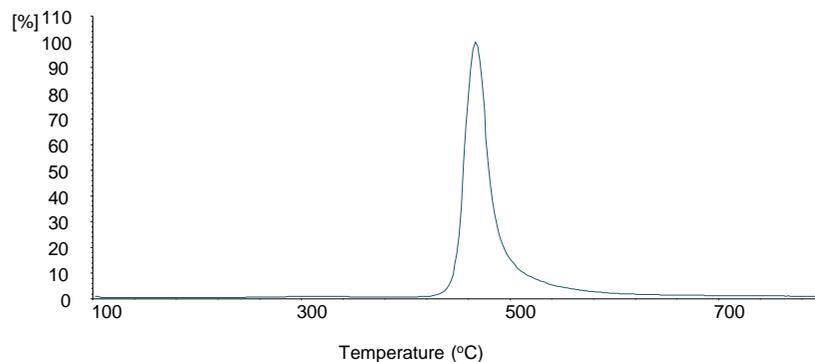
Polyphenylene Ether (PPE) Resins and Filaments

- ❖ **BACKGROUND:** Poly(p-phenylene oxide)(PPO) or poly(p-phenylene ether) (PPE) is a high-temperature thermoplastic. It is rarely used in its pure form due to difficulties in processing. It is mainly used as a blend with polystyrene, high impact styrene-butadiene copolymer or polyamide. PPO is a registered trademark of a commercial Innovative Plastics and is commercially known as Noryl. There is a high interest in using PPO or PPE for 3D Printing. PPE blends are used for structural parts, electronics, household and automotive items that depend on high heat resistance, dimensional stability, and accuracy. They are also used in medicine for sterilizable instruments made of plastic. This plastic is processed by injection molding or extrusion; depending on the type, the processing temperature is 260-300 °C. The surface can be printed, hot-stamped, painted or metalized. Welds are possible by means of heating element, friction or ultrasonic welding. It can be glued with halogenated solvents or various adhesives.
- ❖ **PROBLEM:** Although PPE is a commonly used high performance polymer resin, their properties and formulation chemistry vary with different formulators and manufacturers. While IR spectroscopy can be used for screening, it is not sufficient for composition determination or distinguishing the presence of PPO resins or sources.
- ❖ **SOLUTION:** Perform EGA followed by a single shot analysis to confirm the presence of the PPE or its other polymer contents and the general presence of other additives of a commercial filament.

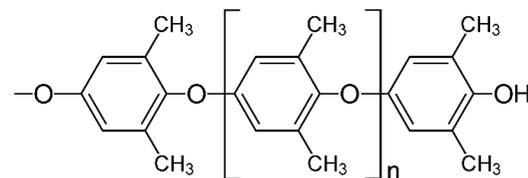
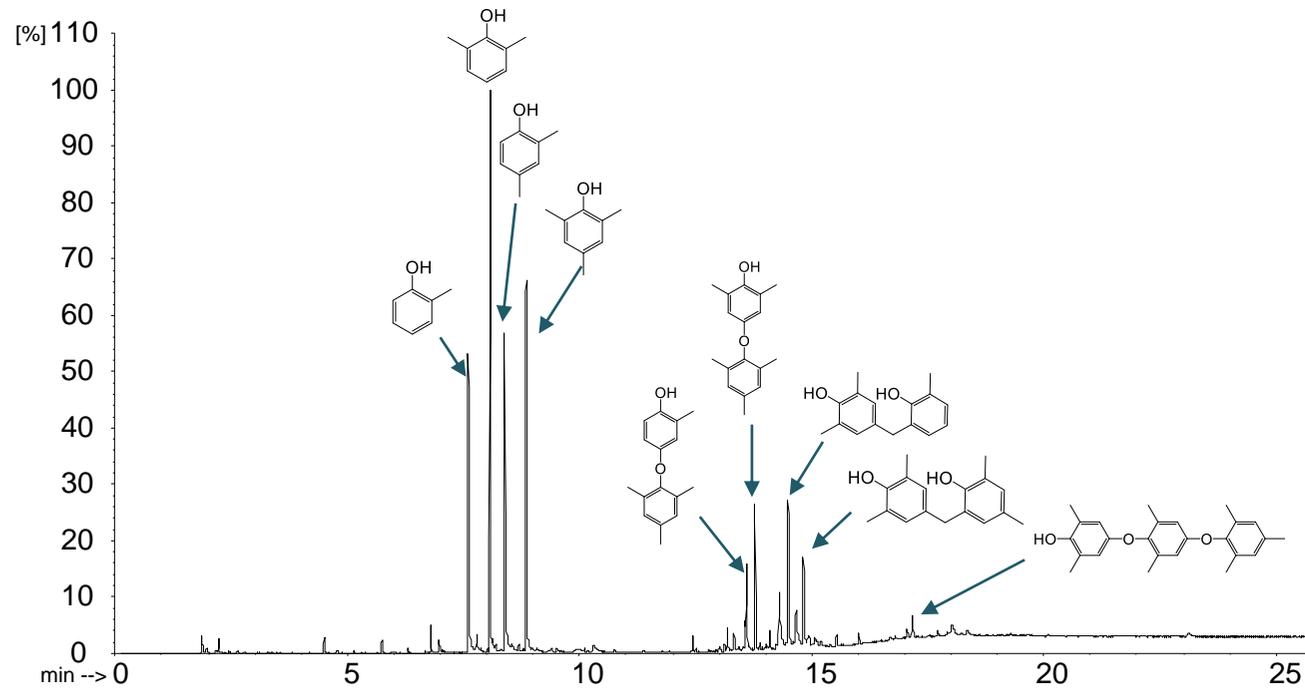


❖ **EXPERIMENTAL:** Around 100 µg of an extruded filament from commercial pellet was cut into an inert Eco-Cup and placed in the auto sampler. To perform EGA, the micro-furnace was then programmed from 100 to 800 °C (20 °C/min). The GC oven was kept isothermal at 320 °C. A single shot analysis was done at 600 °C, determined from EGA thermogram. The oven temperature is programmed to equilibrium at 40 °C for 2 min, increase to 320 °C by 20 °C/min and hold 320 °C for 10 minutes. The result was analyzed by F-search library of component.

❖ **RESULT:** The EGA chromatogram demonstrated the PPE filament starts to degrade at 440 °C and will be totally degraded at 600 °C. The EGA-MS was created by summarize the spectra from 440 °C to 600 °C. Library search is done by F-search, which fits well with the EGA-MS of sample.

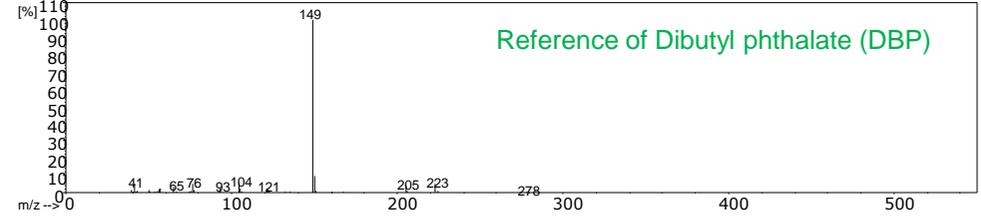
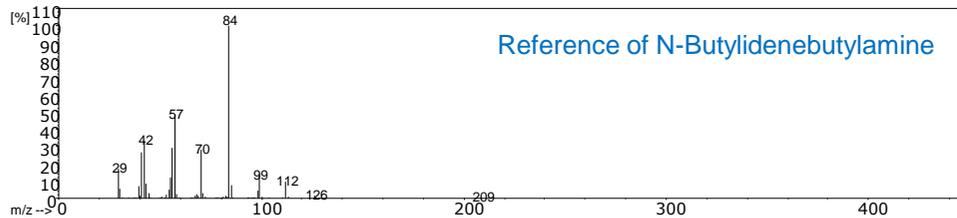
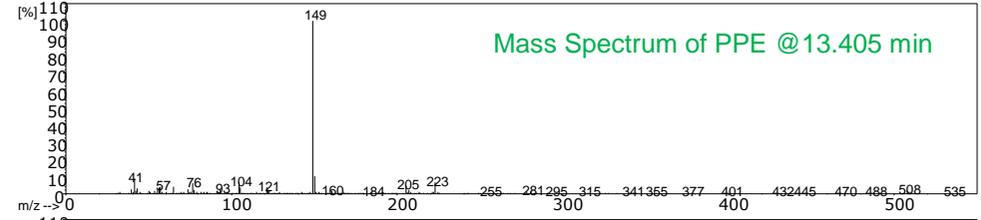
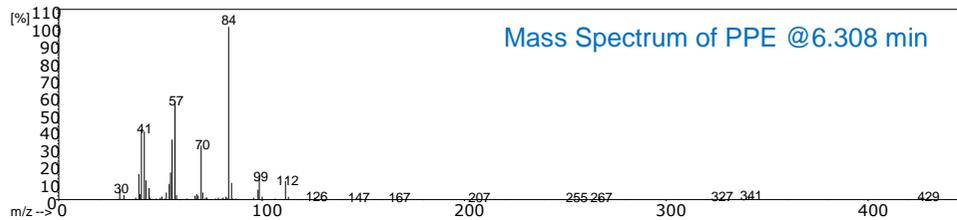
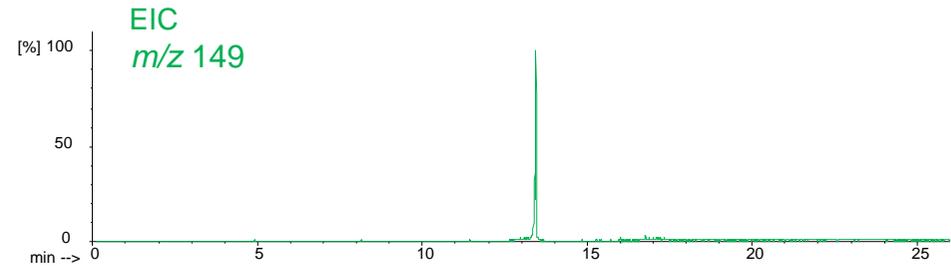
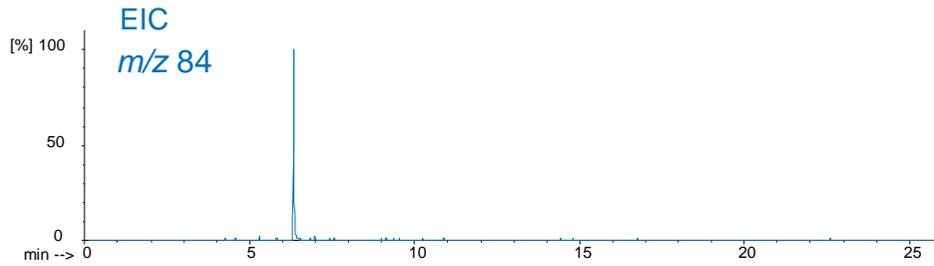
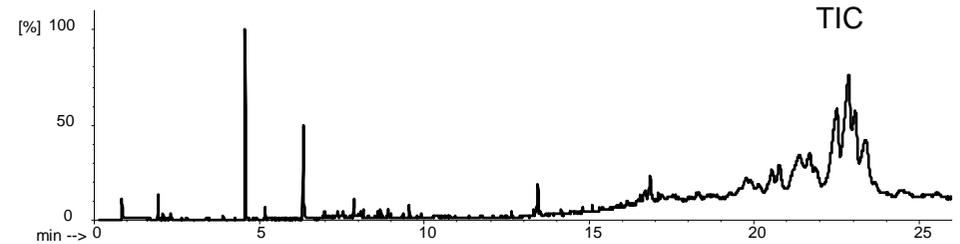


By utilizing pyrolysis at 600 °C, the fragments of PPE filament can be studied. o-Cresol, dimethylphenol and trimethylphenol were detected which suggested the presence of monomer. Dimers were also detected from 10 min to 15 min, while trimers were observed at 17 min. These results proved the presence of PPE polymer.



Polyphenylene ether(PPE)

Thermal Desorption (TD) mode of operation was also used to confirm the presence of two additives. TD was performed from 100 - 380 °C. The Total Ion Chromatogram (TIC) is shown on the right-hand side. Below are the Extracted Ion Chromatograms (EICs) of m/z 84 and m/z 149 indicates N-Butylidenebutylamine and Dibutyle Phthalate (DBP), respectively.



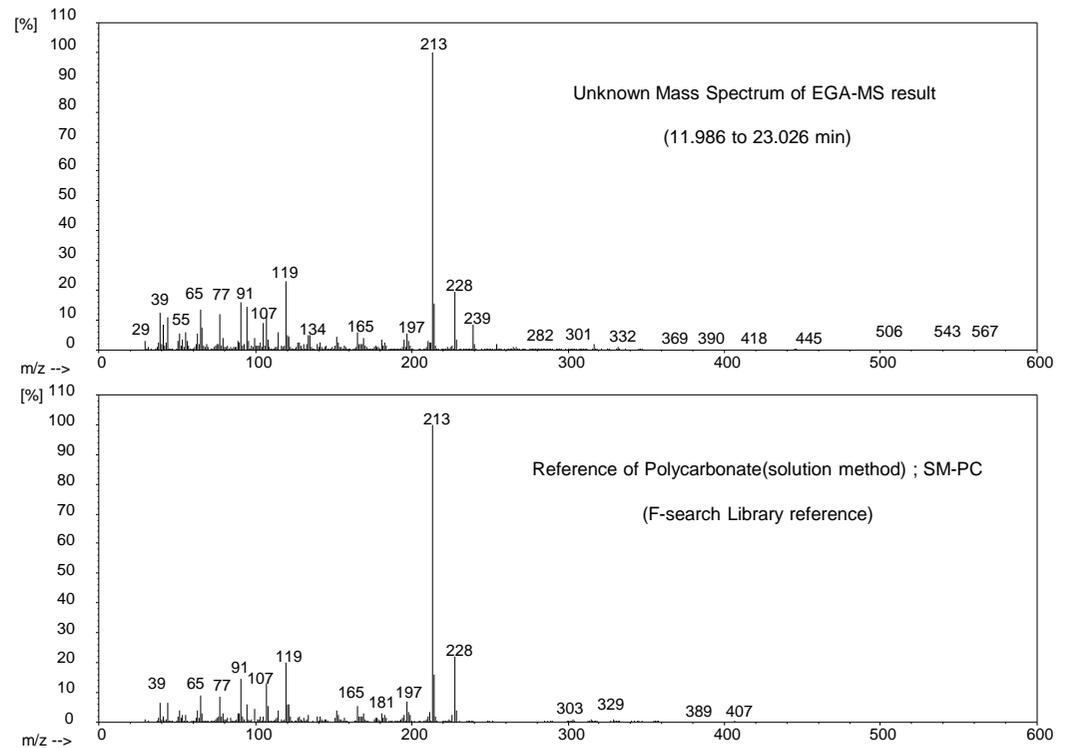
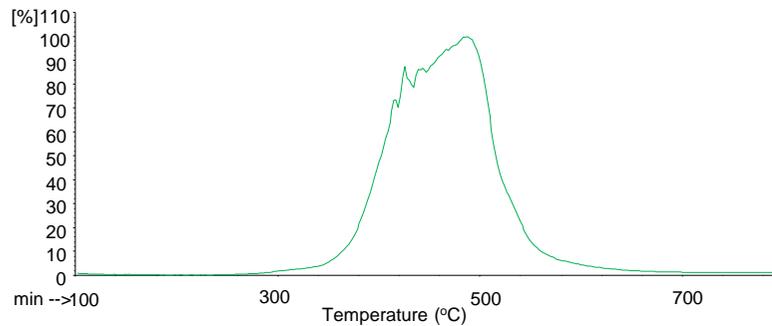
Polycarbonate (PC) Plastic Resins

- ❖ **BACKGROUND:** Polycarbonates (PC) are a group of thermoplastic polymers containing carbonate groups in their chemical structures. Polycarbonates used in engineering are strong, tough materials, and some grades are optically transparent. They are easily worked, molded, and thermoformed. Because of these properties, polycarbonates find many applications. Unlike most thermoplastics, polycarbonate can undergo large plastic deformations without cracking or breaking. As a result, it can be processed and formed at room temperature using sheet metal techniques, such as bending on a brake. Even for sharp angle bends with a tight radius, heating may not be necessary. This makes it valuable in prototyping applications where transparent or electrically non-conductive parts are needed, which cannot be made from sheet metal. This highly desirable engineering polymer material offers excellent chemical resistance and ductile properties suitable for various applications.
- ❖ **PROBLEM:** Although PC is a highly desirable resin, their properties and formulation chemistry vary with different formulators and manufacturers. While IR spectroscopy can be used for screening, it is not sufficient for composition determination or distinguishing the presence of PC resins or sources.
- ❖ **SOLUTION:** Perform EGA followed by a single shot analysis using the Micro-Furnace Pyrolyzer to confirm the presence of the PC or its other polymer contents and the general presence of other additives.

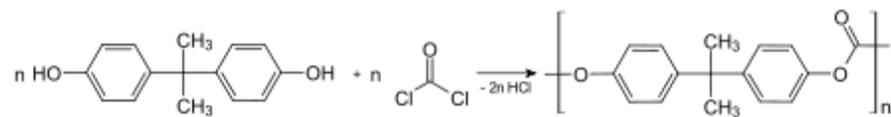
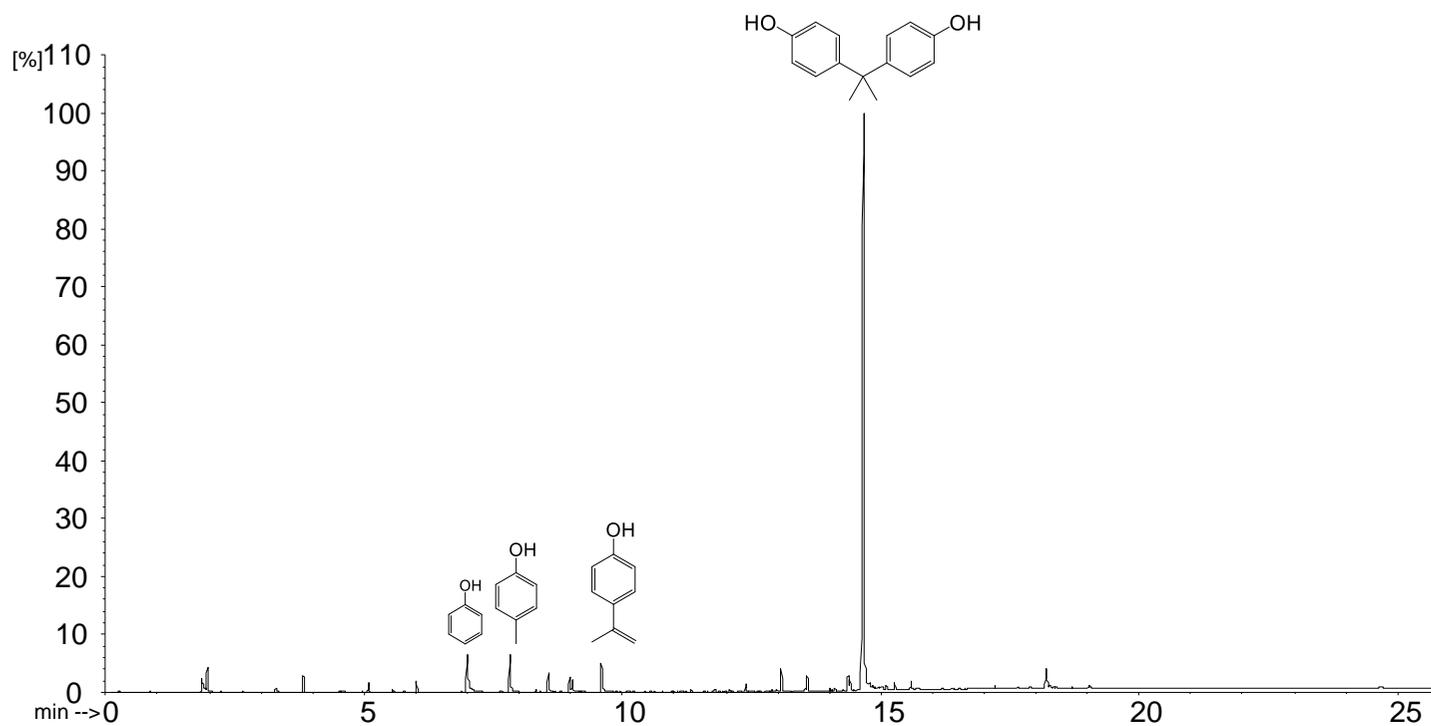


❖ **EXPERIMENTAL:** About 100 µg of commercial PC filament was cut from a commercial PC filament to perform EGA from 100 to 800 °C (20 °C/min). The GC oven was kept isothermal at 320 °C. Flash pyrolysis technique was done using single shot mode at a 620 °C. The oven temperature is programmed to equilibrium at 40 °C for 2 min, increase to 320 °C by 20 °C/min and hold 320 °C for 10 minutes.

❖ **RESULT:** The EGA thermogram demonstrated that the PC filament start to degrade at 320 °C and will be totally degraded at 600 °C. Library search is done by F-search, which fits well with the EGA-MS of sample, giving a result of good fitting with PC reference.



The single shot GC/MS was analyzed by F-search compound library. A major peak of bisphenol A is detected, demonstrating the breaking of ester bonds. Phenol, cresol and isopropylphenol were detected which demonstrate the C-C breaking at higher temperature. This result proves the presence of PC.



Analysis of Gases Released from Heated Food Wrap Films

❖ **PROBLEM:** How can gases released from food wrap films at high temperatures be analyzed?

❖ **SOLUTION:** Using Micro-furnace Multi-Shot Pyrolyzer, evolved gases from various food wrap films that were exposed to 100 °C for 10 min were analyzed.

❖ **RESULT:** Table 1 shows basic polymers of the food wrap films analyzed and organic additives labeled on the package. Fig. 1 shows chromatograms obtained by (TD)-GC/MS analysis of evolved gases collected with MicroJet Cryo-Trap. Upon quantitative analysis, it was found that levels of each component were 100 ppm or less.

Table 1 Additives of Food Wrap Films

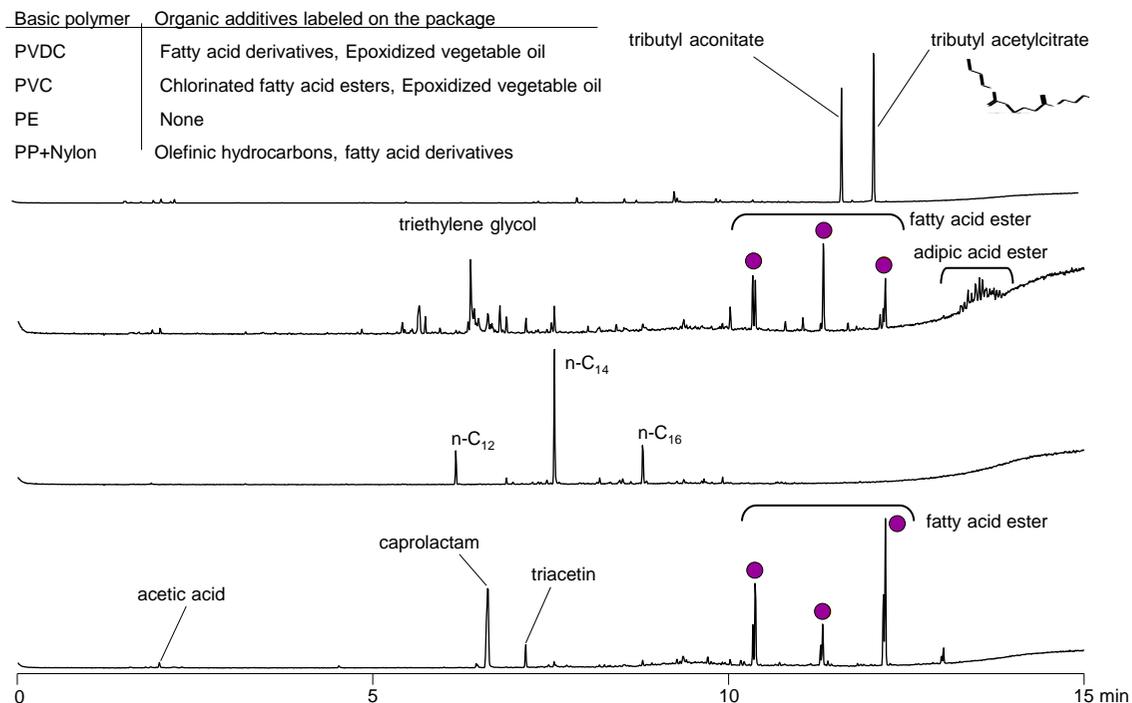


Fig. 1 Chromatograms of Evolved Gases from Food Wrap Films Exposed to 100 °C for 10 min

Pyrolysis temp: 100 °C, Carrier gas: He, column flow rate: 1.0 mL/min, carrier gas total flow rate: 60 mL/min, Cryo trap: 10 min, separation column: Ultra ALLOY+5 (5% diphenyl dimethyl polysiloxane), length: 30 m, id: 0.25 mm, film thickness: 0.25 µm, GC oven temp: 40 - 320 °C (20 °C/min), GC injection port temp: 320 °C, sample: 9 cm², MS scan range: *m/z* 29 - 400, scan rate: 2 scans/sec

Analysis of a Food Wrap Film (Polypropylene and Nylon) using EGA-GC/MS

❖ **PROBLEM:** When heated, volatiles are released from food wrap film (polypropylene + nylon). How can the analysis be performed?

❖ **SOLUTION:** The analysis can be performed using a Multi-Shot Pyrolyzer. Using EGA-MS technique, EGA profile is obtained by programmed pyrolysis from 40 to 600 °C at a ramp rate of 30 °C/min. Then, Zone A and Zone B of the EGA profile are analyzed by (TD)-GC/MS using MicroJet Cryo-Trap.

❖ **RESULT:** Fig. 1 shows the EGA profile acquired using EGA-MS technique. The results of (TD)-GC/MS analysis of Zones A and B obtained utilizing MicroJet Cryo-Trap are shown in Fig. 2. In Zone A, volatile acetic acid, and fatty acids and their derivatives as plasticizer were found. In Zone B, olefinic hydrocarbons of C6, C9, C12, and C15 derived from pyrolysis of polypropylene, and ε-caprolactam, monomer of nylon-6, were observed.

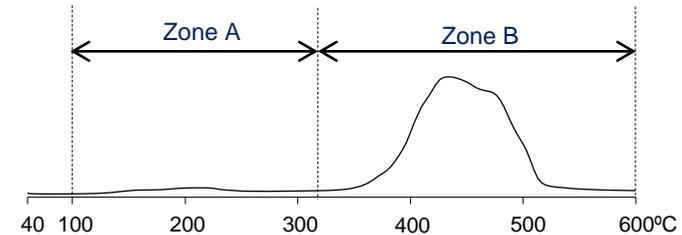


Fig. 1 EGA Profile of Polypropylene + Nylon

Pyrolysis temp: 40 – 600 °C (30 °C/min), carrier gas: He
Interface: deactivated metal capillary column (length: 2.5 m, id: 0.15 mm)
Injection port pressure: 50 kPa

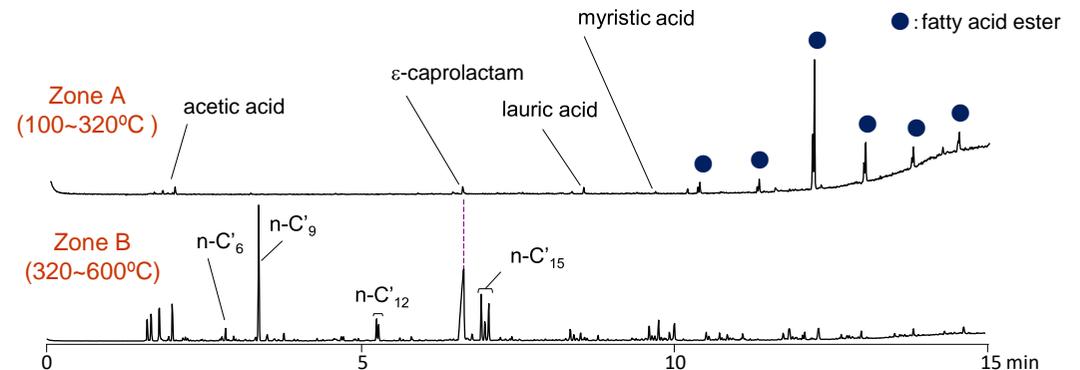


Fig. 2 Analysis Results of Zones A, B, and C of Polypropylene + Nylon

Carrier gas: He, column flow rate: 1 mL/min, total carrier gas flow rate: 40 mL/min, separation column: Ultra ALLOY-5 (5% diphenyl dimethyl polysiloxane), length: 30 m, id: 0.25 mm, film thickness: 0.25 μm, GC oven temp: 40 °C (1 min hold) - 320 °C (20 °C/min), injection port temp: 320 °C, Cryo trap temp: -196 °C, sample: 0.25 cm²

Evaluation of The Aged Deterioration of PE Pipes Used for a Hot-Water Heating System

- ❖ **BACKGROUND:** A variety of additives are added to polymeric materials to suppress the aged deterioration. Information on the degradation of additives over time is useful to evaluate the life of polymer products. Thermal desorption (TD)-GC/MS has been widely used for polymer additive analysis, because cumbersome pretreatments, such as solvent extraction, are not necessary. This note describes the results of TD-GC/MS analysis of the additives contained in cross-linked polyethylene (PE-Xb) pipes which have been exposed to hot water.
- ❖ **EXPERIMENTAL:** TD-GC/MS analysis was carried out using a Py-GC/MS system which consisted of a Multi-Shot Pyrolyzer (EGA/PY-3030D) interfaced directly to the split injection port of a GC/MS system. TD maximum temperature was based on the EGA-MS thermogram. PE-Xb samples were collected by scraping the inner wall surfaces of “new” and “used” pipes, and 1 mg of the sample was placed in a deactivated stainless sample cup.



❖ **RESULT:** The chromatograms of the “new” and “used” PE-Xb samples obtained by TD-GC/MS are shown in Fig. 1. In the “new” PE-Xb pipe, Irgafos 168 (including the oxidized Irgafos 168, phosphate form) and Irganox 1076 are observed, whereas Irgafos 168 and Irganox 1076 are not observed in the chromatogram of the “used” pipe. These results suggest that the additives in PE-Xb pipes are either oxidized or hydrolyzed when exposed to hot water and oxygen over time.

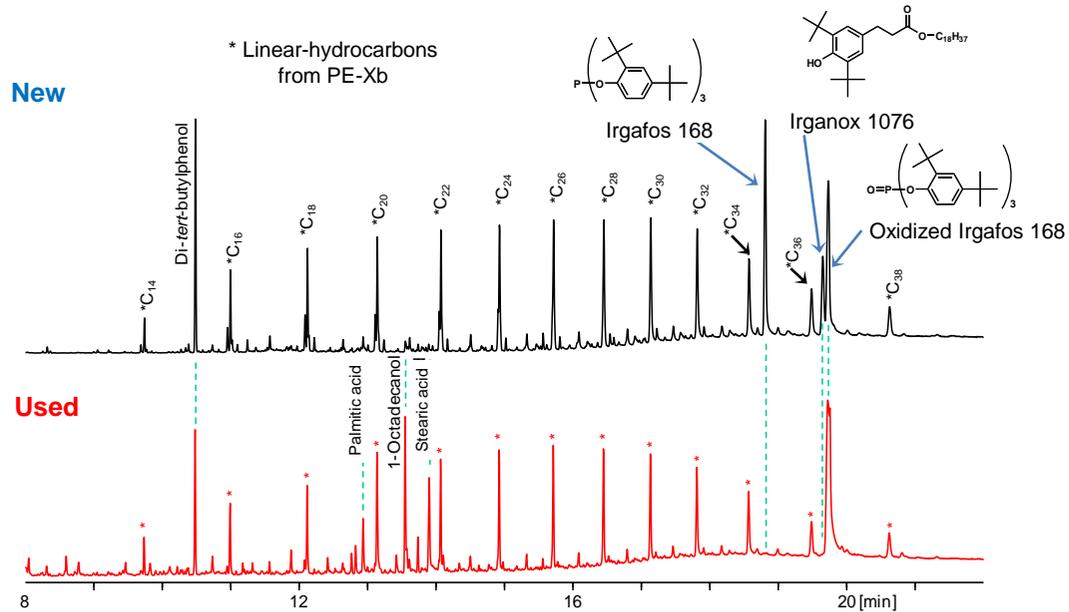


Fig.1 Chromatograms of new and used PE-Xb samples obtained by TD-GC/MS

Furnace temp.: 40 - 350 °C (40 °C/min, 1 min hold), GC oven temp.: 40 (2 min) - 340 °C (20 °C/min, 13 min hold), separation column: Ultra ALLOY+ -5 (5 % diphenyl 95 % dimethylpolysiloxane), $L=30$ m, i.d.=0.25 mm, $df=0.25$ μ m, column flow rate: 1 mL/min He, split ratio: 1/10, sample: 1 mg

Analysis of Thermoset Resin

❖ **BACKGROUND:** The EGA-MS library search is a combination of Evolved Gas Analysis, a thermal analysis technique using multi-mode micro-furnace Pyrolyzer, and mass spectrometry. It is very useful as a primary search technique for unknowns.

❖ **EXPERIMENTAL:** Described here is an analysis example of a thermoset resin. Fig. 1 shows the EGA curve of the thermoset resin and averaged spectra obtained from regions A, B, and C. The result of library search on these spectra using EGA-MS LIB is shown in Table 1.

❖ **RESULT:** Cresol and phenol resins were found in region B, and a cresol resin was found in region C with high quality. Because of low elution temperature of region A, therefore low boiling species, a library search was done using Wiley275, a commonly used MS library and Triphenylphosphineoxide, a reaction catalyst, was found. As described here, EGA-MS technique and library search using EGA-MS LIB are extremely useful for composition analysis of unknown polymer materials as a primary search method.

Table 1 EGA-MS Library Search for Regions B and C

Region B			
	Name	Ref No.	Qual
1.	Cresol formaldehyde resin (Novolak)	#165	53
2.	Cresol formaldehyde resin (Novolak)	#163	53
3.	Phenol formaldehyde resin (Novolak) : PF	#156	32
Region C			
	Name	Ref No.	Qual
1.	Cresol formaldehyde resin (Novolak)	#165	38
2.	Poly-m-phenyleneisophthalamide	#195	16
3.	Poly(phenylene oxide) : PPO	#210	10

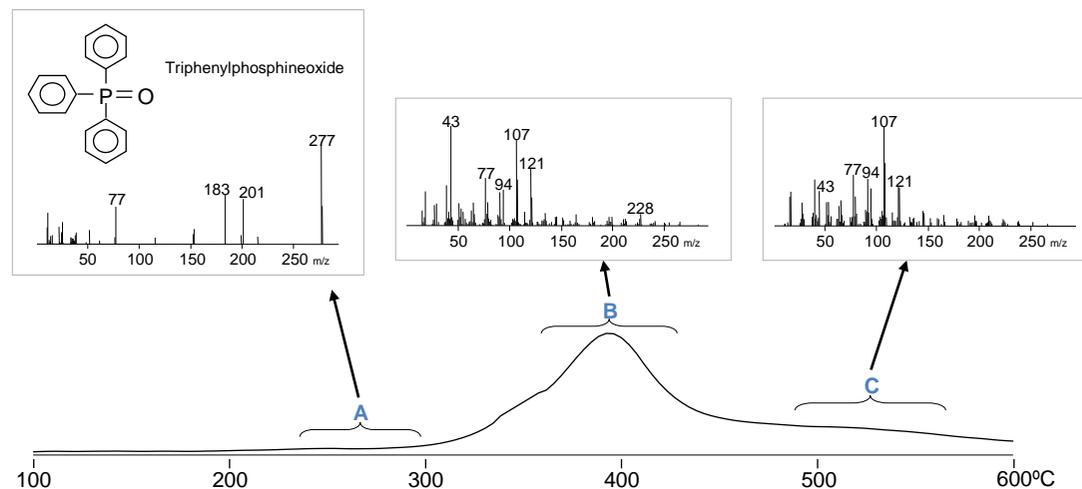


Fig. 1 EGA Curve of a Flame-Retardant Resin

Furnace temp: 100 - 600 °C (20 °C/min), Carrier gas : He 50 kPa, Split ratio : ca. 1/50; EGA capillary tube : 0.15 mm id, 2.5 m (UADTM-2.5N), GC oven temp.: 300 °C; Injection temp.: 320 °C, Sample : ca. 0.5 mg, Detector : MS (m/z 10 - 400, 0.1 scans/sec); PY-GC interface temp.: 320 °C (AUTO mode)

If more than one peak are observed in an evolved gas (EGA) curve, EGA-GC/MS is a useful technique to determine the composition of each peak observed. In this technique, components in each temperature region are introduced into a GC column and temporary trapped at the front of the column using Selective Sampler (SS-1010E) and MicroJet Cryo-Trap (MJT-1030E). They are then separated by GC and finally analyzed by MS.

Using this technique, analysis of components in each peak allows detailed characterization of polymers.

Fig. 2 shows chromatograms of three temperature regions, A, B, and C observed in the EGA curve of a thermoset resin. Triphenylphosphineoxide, a reaction catalyst, was found in peak A, while various phenols, thermal decomposition products of phenol resin, and styrene monomer, thermal decomposition product from polystyrene, were found in peaks B and C.

As shown here, analysis of each temperature region of an EGA Curve offers detailed information on polymers.

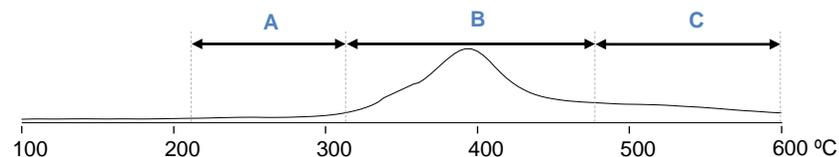


Fig. 1 EGA Curve of a Flame-Retardant Resin

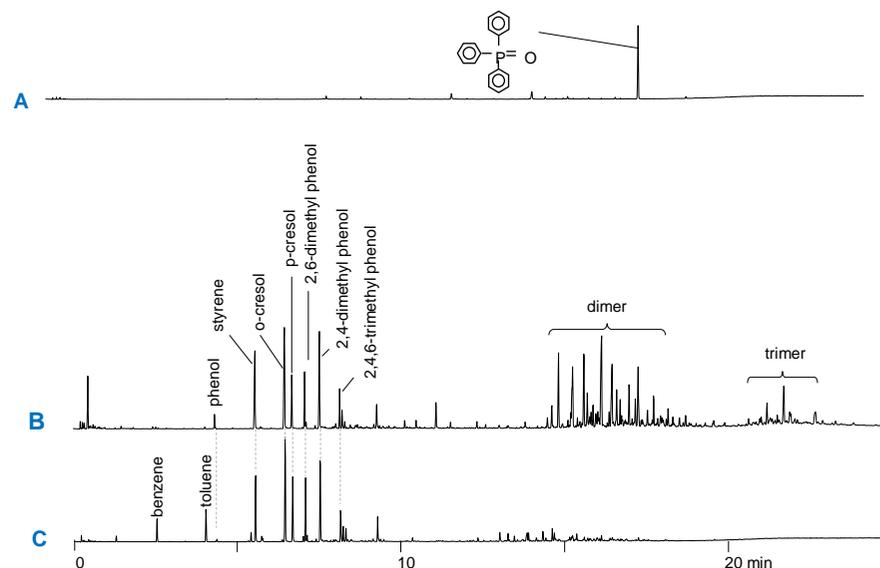


Fig. 2 Chromatogram of Each Temperature Region of EGA Curve

Separation column : Ultra ALLOY+-5 (5% diphenyl polysiloxane) 30 m, 0.25 mm id,
 Film thickness : 0.25 μ m; Sample : 500 μ g, Detector : MS (m/z 10 - 400, 2 scans/sec)

Analysis of Additives in Polybutylene Terephthalate (PBT)

❖ **BACKGROUND:** For electronic applications, polyolefin modifier is often added to Polybutylene terephthalate (PBT) resin to improve hydrolysis and thermal shock resistances. It is of importance to analyze additives in PBT resin in order to ascertain its performance.

❖ **EXPERIMENTAL:** Here, a new analysis technique, which is a combination of Double-Shot and reactive pyrolysis, is described. In the first step, a pyrogram was obtained by reactive pyrolysis of PBT at 400 °C in the presence of tetra-methyl ammonium hydroxide (TMAH) (Fig. 1). In the second step, a pyrogram was obtained by instant pyrolysis of residual polyolefin modifiers at 550 °C (Fig. 2).

❖ **RESULT:** A methyl derivative of terephthalic acid, a constituent monomer of PBT, was observed in the first step; and sets of 3 peaks for straight chain hydrocarbons of diolefins, olefins, and paraffin were observed in the second step. These results demonstrated that polyolefin additives in the PBT resin could be separated and identified using this technique.

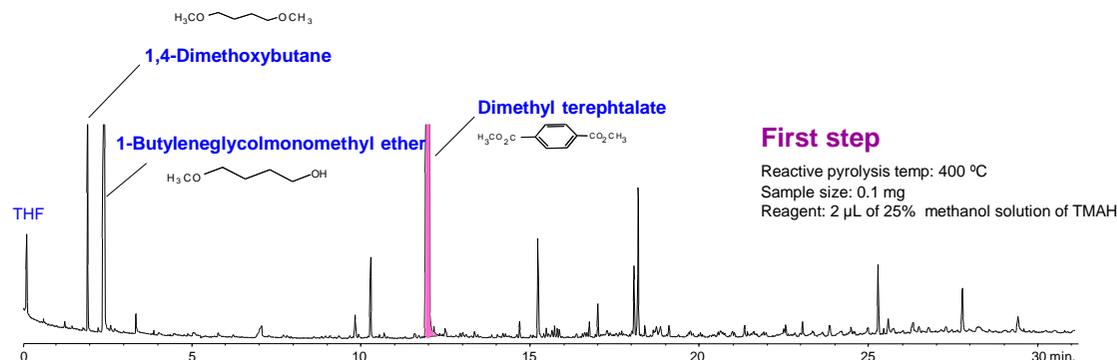


Fig. 1 Pyrogram Obtained by Reactive Pyrolysis of PBT

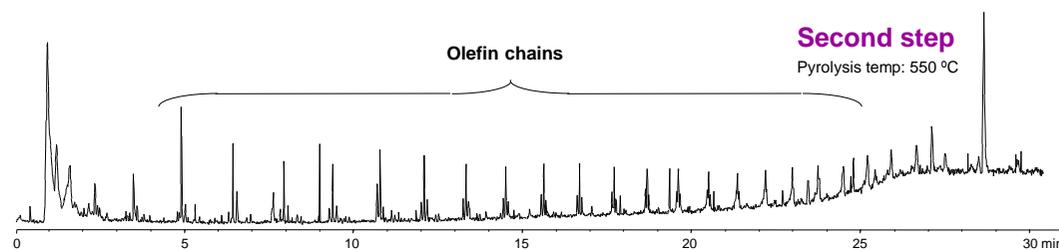


Fig. 2 Pyrogram of Residue (550 °C)

Analytical conditions: carrier gas: He, Injection port pressure: 103 kPa, Split ratio: 1/60, Separation column: Ultra ALLOY⁺-5 (5% diphenyldimethylpolysiloxane); Length: 30 m, Id: 0.25 mm, Film thickness: 0.25 μm, GC oven temp: 38 °C - 300 °C(20 °C/min), GC injection port temp: 320 °C

Determination of Phthalates in PVC by Thermal Desorption-GC/MS

Part 1: Determination of the thermal desorption temperature zone by EGA

- ❖ **BACKGROUND:** Phthalates are widely used in the plastic industry; the six phthalates listed in Table 1 are regulated by the EU and the US when used in toys and other childcare products. In Japan, the Health, Labor and Welfare Ministry guideline No.336 issued on September 6, 2010 regulates the six phthalates listed in Table 1; consequently, the analysis of phthalates is becoming commonplace and there is a near universal interest in a simple, accurate method for analyzing phthalates in polyvinyl chloride (PVC).
- ❖ **PROBLEM:** Traditional (e.g. solvent extraction, filtration, etc.) sample preparation techniques are cumbersome, time consuming and suffer from analyst-to-analyst variability.
- ❖ **SOLUTION:** Thermal desorption (TD)-GC/MS is a simple, one-step technique which is suited for the analysis of phthalates in PVC. PVC often contains a large amount of other plasticizers (several tens of percent) which co-elute with the phthalates of interest. This so-called matrix interference many lead to either false positives or false negatives. In addition, matrix interference makes an accurate determination of the co-eluting phthalates problematic, at best. This technical note describes how Evolved Gas Analysis (EGA) – MS is used to define the optimal thermal desorption temperature zone for the phthalates of interest.



❖ **EXPERIMENTAL:** A sheet of PVC containing DINCH at 40% (Fig. 1) and six restricted phthalates at 0.1% each was analyzed. Small pieces (~ 20 mg) sampled from several different locations were dissolved in 1 mL of THF (20 mg/mL). 10 µL of the solution was placed in a sample cup and the solvent evaporated leaving a thin film of the sample on the surface of the cup. EGA-MS analysis was performed on this sample using a Multi-shot pyrolyzer: EGA/PY-3030D.

❖ **RESULT:** The EGA thermogram of the PVC sheet is shown in Fig. 2. It contains peaks originating from the plasticizers, HCl (thermal decomposition of PVC), and aromatic compounds (which are attributed to the thermal decomposition of polyenes upon the dehydro-chlorination of PVC). Characteristic ions for DINCH, HCl, and the phthalates of interest are used to define the optimal thermal desorption zone: 100 - 320 °C.

Table 1. Restricted phthalates
(0.1 % upper limit by Directive 2005/84/EC)

Di(2-ethylhexyl)phthalate (DEHP)
Dibutylphthalate (DBP)
Butylbenzylphthalate (BBP)
Diisononylphthalate (DINP)
Diisodecylphthalate (DIDP)
Di(n-octyl)phthalate (DNOP)

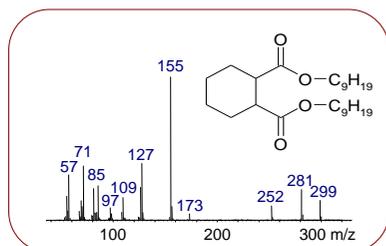


Fig 1. DINCH: 1,2-Cyclohexane dicarboxylic acid di-isononyl ester

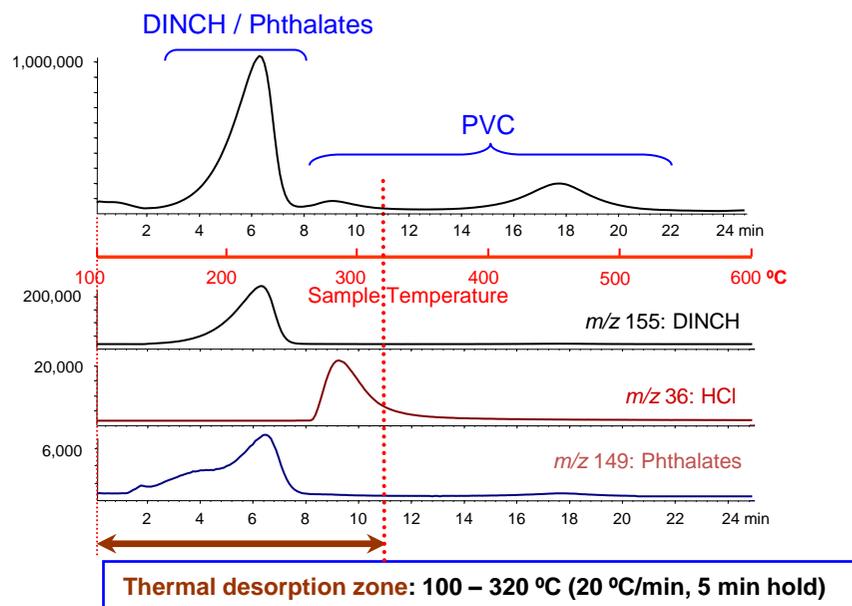
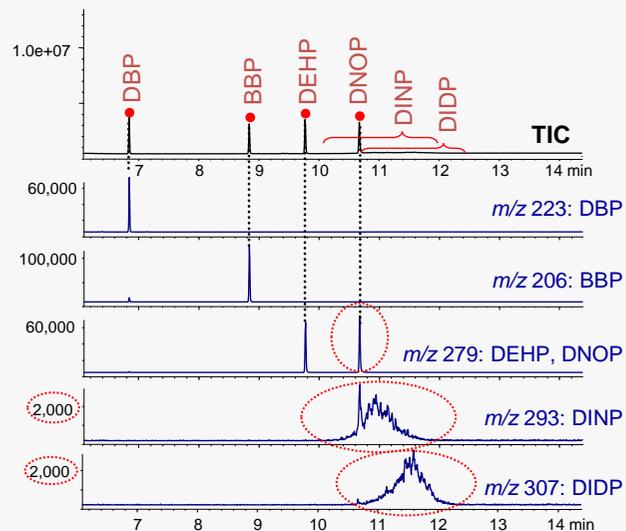


Fig. 2 EGA thermogram and mass fragmentgrams of PVC sample

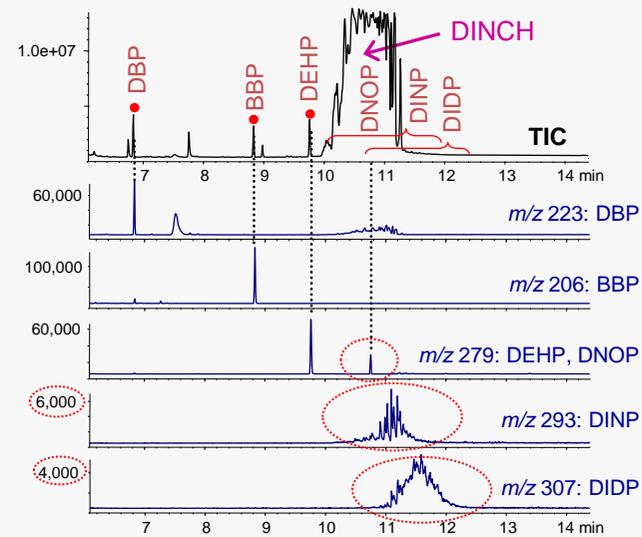
Determination of Phthalates in PVC by Thermal Desorption-GC/MS

Part 2: Calibration using absolute calibration method and standard addition

- ❖ **BACKGROUND:** Using the thermal desorption temperature zone described in the previous page, two different calibration methods (absolute calibration and standard addition) were evaluated in order to determine which method most effectively reduces or eliminates the matrix effects caused by the presence of a large amount of plasticizers in the sample.
- ❖ **EXPERIMENTAL:** The thermal desorption (TD)-GC/MS system consisted of a Multi-shot Micro-furnace pyrolyzer (EGA/PY-3030D) interfaced directly to the split/splitless injection port of a GC/MS. A thin film (0.2 mg) of the PVC-DINCH sample was prepared as described in the previous page. The thermal desorption temperature zone was 100 – 320 °C. A calibration standard (Ph-Mix) containing 0.1% of each phthalates was used. Identification was based on the retention time of each phthalate's characteristic ion and the common m/z 149 ion. Quantitation was based on the peak area of the characteristic ion.
- ❖ **RESULT:** No DINCH interferences were observed for DBP, BBP, and DEHP, and both methods gave similar results – Fig.1. However, DNOP, DINP, and DIDP co-elute with the DINCH peak envelop which potentially will degrade the accuracy of the phthalate concentration determination. Specifically, if there is no DINCH in the sample, the retention time of DNOP shifts and the peak width at half-height is double what it is when the sample contains DINCH. In addition, the peak height is 60% lower when DINCH is present; consequently, when the absolute calibration method is used, the concentrations of DNOP, DINP, and DIDP are higher than the true value of 0.1%. On the other hand, the concentration of the phthalates obtained using the standard addition method are very close to the true value of 0.1%. The results show that standard addition is the preferred method when quantitating phthalates in PVC using TD-GC/MS. Standard addition minimizes the interference when high concentrations of plasticizers which co-elute with the phthalates of interest are present.



(a) Ph-Mix (0.1% each)



(b) PVC-DINCH (Contains 0.1% each Ph)

Fig.1 TD chromatograms of samples and effects of DINCH interference to phthalates (TD: 100 - 320 °C/min, 5 min hold)

Phthalate: 0.1% each		DBP	BBP	DEHP	DNOP	DINP	DIDP
%RSD (n=5)		0.79	0.85	0.69	1.59	1.59	0.98
Quantified value (%)	Absolute calibration	0.122	0.117	0.121	0.029	0.126	0.193
	Standard addition	0.115	0.093	0.096	0.098	0.103	0.088

Effects of Thermal Desorption Temperature for Phthalates in PVC

- ❖ **PROBLEM:** When phthalates in plastic toys are analyzed using thermal desorption (TD)-GC/MS, does the sample form influence the reproducibility?
- ❖ **EXPERIMENTAL:** Solid samples were milled to 45 mesh, and thin films were prepared by solvent casting, and were analyzed by (TD)-GC/MS. The thermal desorption zone for the phthalates was determined to be 100 - 350 °C. The levels of the phthalates were calculated using an absolute area calibration.
- ❖ **RESULT:** Fig. 1 shows a TIC chromatogram obtained by (TD)-GC/MS. DINCH, a non-phthalate plasticizer, was identified as the major component in the 17 - 18 minutes retention window. Compounds having fragment ions m/z 149, 223, 273 were found at 11 and 16 min, and based on the mass spectra and retention times, these peaks are identified as DBP and DEHP. The concentrations of these phthalates are ca. 50 and ca. 300 ppm, respectively. The reproducibility ($n=5$) of the DEHP concentration was 5% RSD for the powder, and 1% for the thin film. The difference between the two can be attributed to the lack of homogeneity of the solid sample.

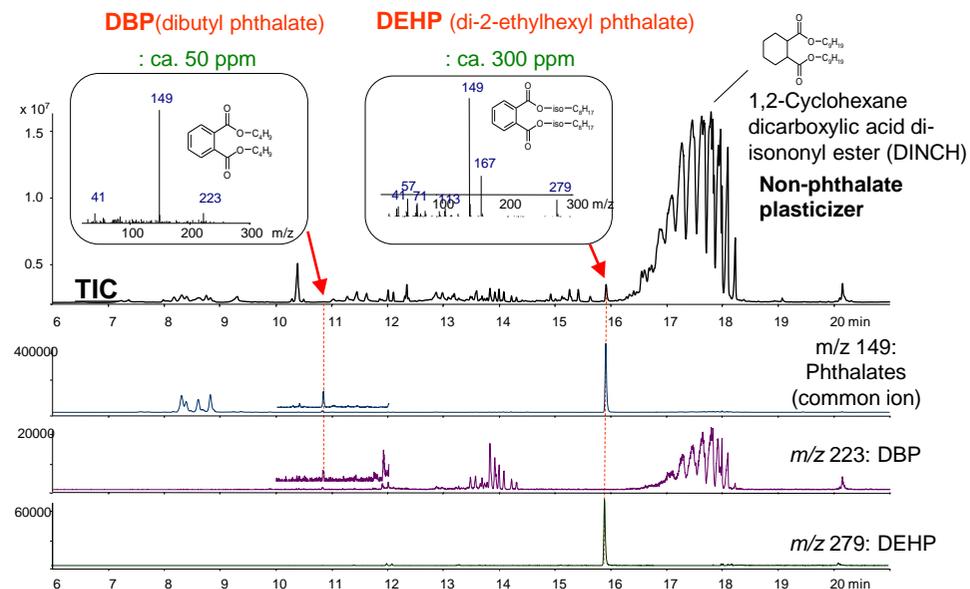


Fig. 1 TIC and extracted ion chromatograms of a PVC sample obtained by TD-GC/MS

Thermal desorption temp: 100 - 350 °C (40 °C/min, 3 min), GC oven temp: 80 - 320 °C (10 °C/min, 6 min), Separation column*: Ultra ALLOY+1 (polydimethylsiloxane, L=30 m, i.d.= 0.25 mm, df=0.05 µm), Column flow rate: 1 mL/min He, Split ratio: 1/20

* For separation column, please use Ultra ALLOY+5 (5% diphenyl 95% dimethylpolysiloxane, L=30 m, i.d.=0.25 mm, df=0.25µm).

Differentiation of DOTP and DNOP in Analysis of Restricted Phthalate Esters Using Thermal Desorption GC/MS

- ❖ **BACKGROUND:** Thermal desorption (TD)-GC/MS is a simple analytical method for the determination of restricted phthalates in polymers. ASTM D7823-18 utilizes TD-GC/MS to determine six restricted phthalates in PVC. D7823-18 uses retention times and mass spectra for the identification of phthalates; therefore, attention must be given to similar compounds having similar retention indices and mass spectra. Miss-identification will result in a false positive and an elevated concentration for the target phthalate. One such example is the possible miss-identification of di-(n-octyl) phthalate (DNOP, CAS: 117-84-0) and bis (2-ethylhexyl) terephthalate (DOTP, CAS: 6422-86-2). Both have m/z 149 and 279 - ions that are used to identify and quantitate DNOP. This technical note shows that these two phthalates are differentiated using the standard GC method described in ASTM 7823-18.
- ❖ **EXPERIMENTAL:** 70 μg of PVC containing tens of % of DINCH and hundreds of ppm of DNOP and DOTP was placed in a sample cup and analyzed using the conditions described in ASTM D7823-18. The Multi-Shot Micro-Furnace Pyrolyzer (EGA/PY-3030D) was directly interfaced to the injection port of the GC/MS system.
- ❖ **RESULT:** DNOP and DOTP co-elute with DINCH (see Fig. 1) which precludes the positive identification and quantitation of either phthalate using the TIC. The mass spectra of both DNOP and DOTP have 149 and 279 ions – see Fig. 2, and therefore extracted ions chromatograms (EIC) cannot be used to differential DNOP and DOTP. On the other hand, m/z 261 is a significant ion in the DOTP mass spectrum. As demonstrated here, the retention time and the presence or absence of m/z 261 ion can be used to differentiate between DNOP and DOTP.

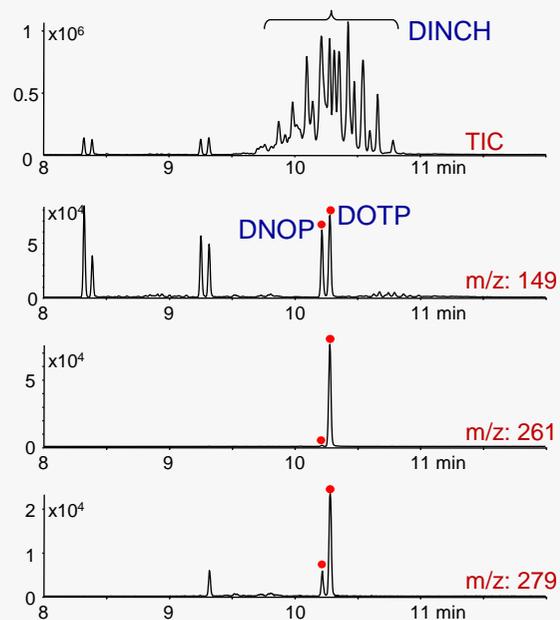


Fig. 1 Chromatograms of a PVC which contains various plasticizers obtained by TD-GC/MS

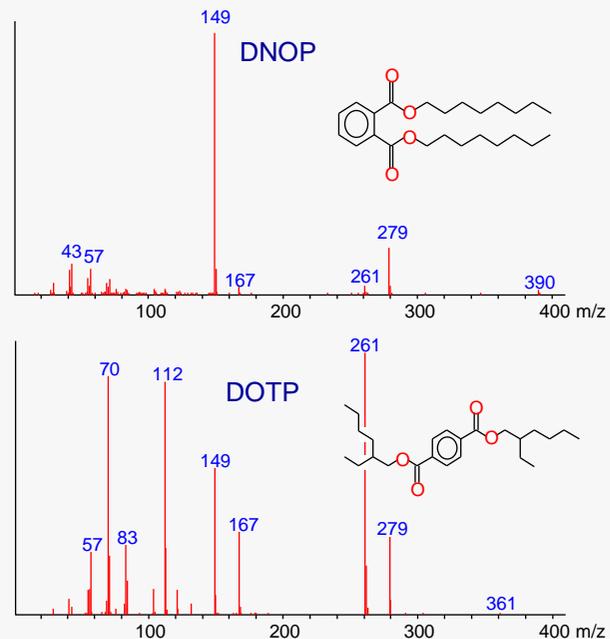


Fig. 2 Mass spectra of DNOP and DOTP

TD: 100 - 320 °C (20 °C/min, 5min hold), GC oven: 80 - 200 °C (50 °C/min) - 320 °C (15 °C/min, 2 min hold)
 Separation column: Ultra ALLOY⁺-5 (5% diphenyl 95% dimethylpolysiloxane)
 L=30 m, i.d.=0.25 mm, df=0.25 µm, split ratio: 1/100, sample wt.: approx. 70 µg

Determination of Antioxidants (Irganox 1076 and Irganox 1010) in Polyethylene – Part 1

❖ **BACKGROUND:** Plastic products often contain a number of additives which give the products desirable physical and chemical properties. Irganox 1076 and 1010 are sterically hindered phenolic antioxidants and are widely used in the formulations of plastics, lubricants, adhesives and car parts. Irganox 1076 in polyethylene (PE) is determined using thermal desorption (TD)-GC/MS. Irganox 1010 in PE can be hydrolyzed and methylated using tetramethyl ammonium hydroxide (TMAH). The methyl derivative has a much lower boiling point and it can be easily vaporized and determined using GC/MS.

❖ **EXPERIMENTAL:** PE-pellets, spiked with either Irganox 1076 (340 ppm) or Irganox 1010 (470 ppm), were pulverized. The spiked PE samples containing Irganox 1076 and Irganox 1010 were respectively analyzed by TD-GC/MS and reactive pyrolysis (RxPy)-GC/MS. In RxPy-GC/MS, TMAH was added to the sample cup containing the spiked PE prior to analysis. Standard addition method was used to generate calibration curves. The analysis was done using a Multi-Shot Pyrolyzer (EGA/PY-3030D) which was directly interfaced to the split injector of a GC/MS system.

❖ **RESULT:** TD chromatogram of PE containing Irganox 1076 is shown in Fig. 1a. The large peak at 26.8 min is assigned as Irganox 1076. Figure 1b shows the total ion chromatogram of PE containing Irganox 1010 treated by hydrolysis and methylation using TMAH. The large peak at 17.9 min is assigned as the methyl derivative of Irganox 1010. Using the standard addition method, the concentrations of Irganox 1076 and Irganox 1010 were respectively determined to be 374 ppm (10% error) and 429 ppm (9% error).

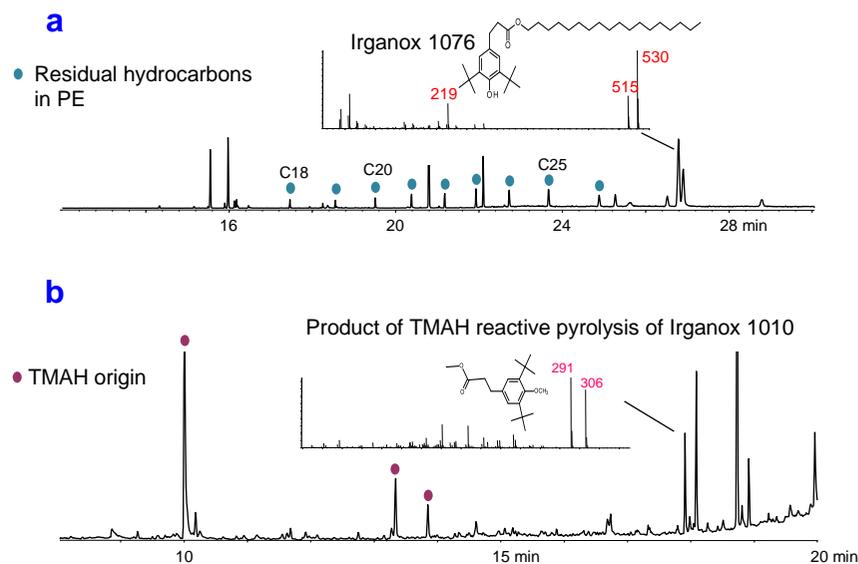


Fig. 1 a: Chromatogram of PE with Irganox 1076 obtained by thermal desorption
 b: Pyrogram of PE with Irganox 1010 obtained by reactive pyrolysis

Furnace temp.: 260 °C (reactive pyrolysis), 320 °C (thermal desorption); GC oven: 40 - 150 °C (10 °C/min) - 320 °C (20 °C/min, 3 min hold); Separation column: Ultra ALLOY+5 (5% diphenyl 95% dimethylsiloxane), L=30 m, i.d.=0.25 mm, df=0.25 µm; Split ratio: 1/30, Sample wt.: approx. 100 µg, 25 wt% TMAH methanol solution: 20 µL

Determination of Antioxidants (Irganox 1076 and Irganox 1010) in Polyethylene – Part 2

❖ **BACKGROUND:** 1010 (MW 1178) and Irganox 1076 (MW 530) have been used as an antioxidant in polymeric materials. Determination of each antioxidant in polyethylene (PE) was reported previously, where Irganox 1010 was determined by reactive pyrolysis (RxPy)-GC/MS with tetramethylammonium hydroxide (TMAH) and Irganox 1076, by thermal desorption (TD)-GC/MS. Both of these antioxidants are sometimes co-added in polymeric materials, and it is not easy to determine each antioxidant in such polymeric materials because both antioxidants give the same reaction product by RxPy-GC/MS with TMAH as shown in Fig. 1. Individual concentration of antioxidants in a PE sample containing both antioxidants can be determined according to the analytical protocol given in Protocol part 1.

❖ **EXPERIMENTAL:** The analytical data was obtained using a Multi-Shot Pyrolyzer (EGA/PY-3030D) interfaced directly to the injection port of a GC/MS system. Analytical conditions including amounts of sample and reagent used are identical to those described in the previous page.

❖ **RESULT:** The concentrations of Irganox 1010 and Irganox 1076 contained in the PE sample was determined to be 1406 ppm (formulated as 1000 - 1500 ppm) and Irganox 1076 was 476 ppm (formulated as 450 - 550 ppm), respectively.

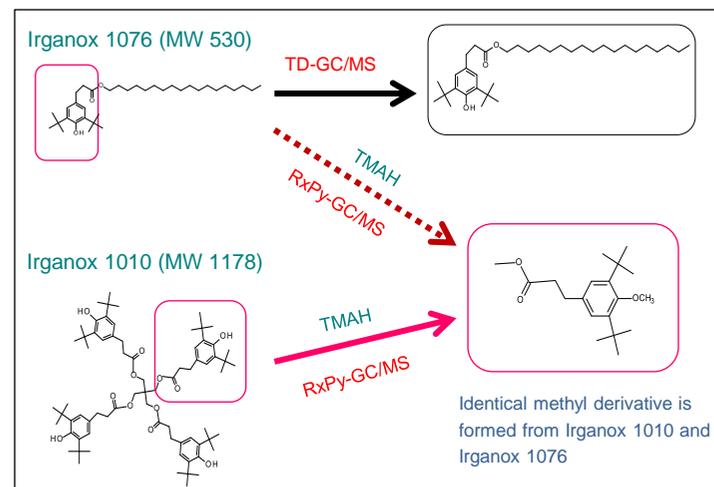
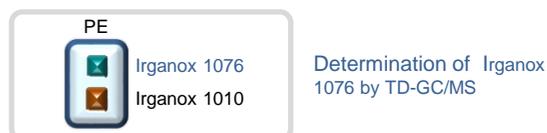


Fig. 1 Methyl derivative of Irganox 1010 and Irganox 1076

❖ **PROTOCOL 1:** Analytical protocol for the determination of Irganox 1076 and Irganox 1010 co-added in PE.

1. TD-GC/MS is used to determine Irganox 1076 in a PE sample containing both antioxidants.



2. The methyl derivative of Irganox 1076 produced by RxPy with TMAH is determined by the standard addition of Irganox 1076 to the PE sample containing Irganox 1076 only (Fig. 2), and the determined value is correlated with the concentration of Irganox 1076 obtained in the step 1.

3. By the standard addition of Irganox 1010 to the PE sample containing both antioxidants, concentration of the methyl derivative produced by RxPy with TMAH is determined (Fig. 2). The determined concentration corresponds to the sum of concentrations of Irganox 1010 and Irganox 1076.

4. By subtracting the concentration of Irganox 1076 determined in the step 2 from the sum of concentrations determined in the step 3, the concentration of Irganox 1010 can be determined.

$$PA_{(1010) Me} = PA_{(1010 + 1076) Me} - PA_{(1076) Me}$$

PA: Peak area

PA_{Me}: Peak area of the methyl derivative

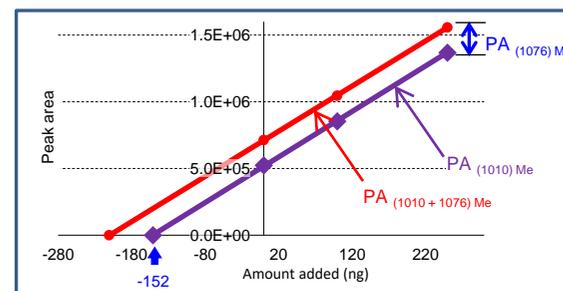


Fig. 2 Calibration curves for the methyl derivative of Irganox 1010

Quantitative Analysis of Phthalate Bis(2 - Ethylhexyl) Phthalate (DEHP) in Heat Resistant PVC Sheath

- ❖ **BACKGROUND:** Phthalate esters are added to PVC formulations to improve the processability and the performance of the PVC. Recently many of these phthalates have been found to adversely affect human health and their use has been restricted or in some cases banned. Bis(2-ethylhexyl) phthalate (DEHP) is among the first six compounds that the EU is phasing out under its REACH program. There are more than 17 analytical methods currently being used to measure DEHP in PVC. With two exceptions, the analysis begins with a cumbersome, time consuming liquid/ liquid extraction. This technical note uses the ASTM Method: D-7823-18 which utilizes thermal desorption (TD)-GC/MS. The method is simple to use and has proven to yield superior precision and accuracy values when compared to those obtained using solvent extraction. This note describes the quantitative TD-GC/MS analysis of DEHP in the outside sheath of commercial-grade cable.
- ❖ **EXPERIMENTAL:** TD-GC/MS system consisted of a Micro-Furnace Multi-Shot pyrolyzer (EGA/PY-3030D) interfaced directly to a GC/MS split injection port. 500 µg of a PVC thin film was placed in an inert SS sample cup. The TD was done as described in the ASTM method. The concentration of DEHP was calculated using an absolute area calibration curve method (m/z 279). The ASTM method requires that quantization to be done using standard addition because of the possible interference from other plasticizers (e.g., DINCH) in the PVC. In this case the plasticizers were trimellitate and adipates and there was no interference with the DEHP ions.
- ❖ **RESULT:** A typical total ion chromatogram (TIC) and extracted ion chromatograms (EICs) of the PVC sample are shown in Fig.1. m/z 149 and 279 are used to confirm the presence of DEHP. Two positional isomers of DEHP (regioisomers), tris(2-ethylhexyl) trimellitate (TOTM) and TOTM anhydride are also present. Quantification was performed using the calibration curve shown in Fig.2. The concentration of DEHP in this PVC sample was found to be 245 ppm ($n=3$, RSD=0.7%).

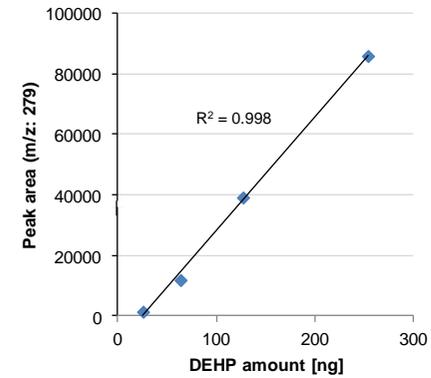
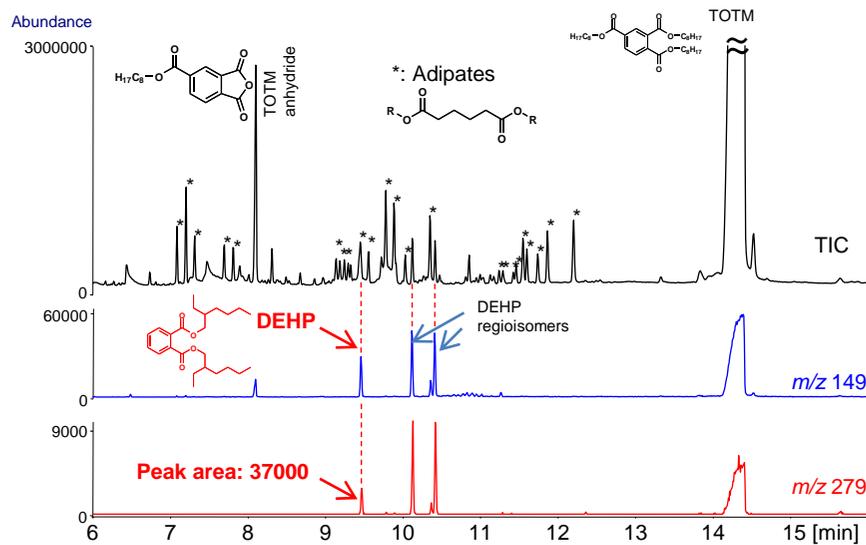


Fig.2 Calibration curve of DEHP

Fig.1 TD-GC/MS chromatogram and extracted ion chromatograms of heat resistant PVC

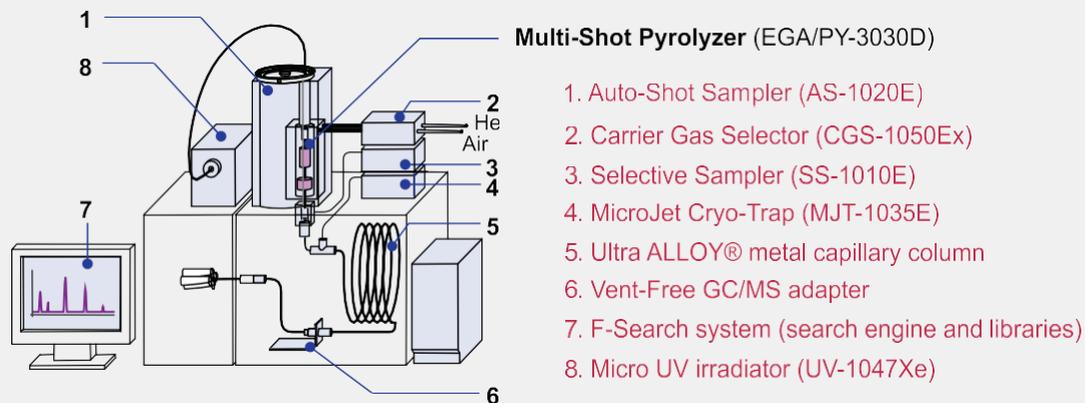
TD temp.: 100 - 320 °C (20 °C/min, 1 min hold), GC oven temp.: 80 (2 min) - 200 °C (40 °C/min) - 320 °C (15 °C/min, 3 min hold)
 Separation column: Ultra ALLOY⁺-5 (5 % diphenyl 95 % dimethylpolysiloxane, L=30 m, i.d.=0.25 mm, df=0.25 μm)
 Column flow rate: 1.2 mL/min He, Split ratio: 1/50, Sample wt: ca. 500 μg

What is Pyrolysis GC/MS Technique?

Pyrolysis GCMS is a powerful and straightforward technique that utilizes a Frontier Micro-Furnace Pyrolyzer as a programmable temperature inlet to a Gas Chromatography-Mass Spectrometer (GCMS) system. The material of interest (liquid or solid) is uniformly heated in an inert atmosphere. Volatile organics evolve at temperatures below 300 °C. At higher temperatures, covalent bonds break, and the complex structure is degraded into smaller (stable and volatile) molecules which are referred to as pyrolyzates. The pyrolyzates formed and their relative intensities provide insight into the structure of the original material.

The Frontier Pyrolyzer is interfaced directly to the GC inlet. The sample is placed in a small deactivated cup which is, in turn, positioned in a micro-furnace. The temperature of the sample is carefully controlled (± 0.1 °C) to ensure that the sample-to-sample thermal profile is identical. Frontier's well-engineered technology ensures that the sample is maintained at ambient temperature, in an inert atmosphere, prior to pyrolysis; thus eliminating evaporation, thermal degradation, and thermosetting before analysis.

The technical data in this monograph were obtained using one or more of the listed accessories. Each accessory is described in more detail in the system configuration section.

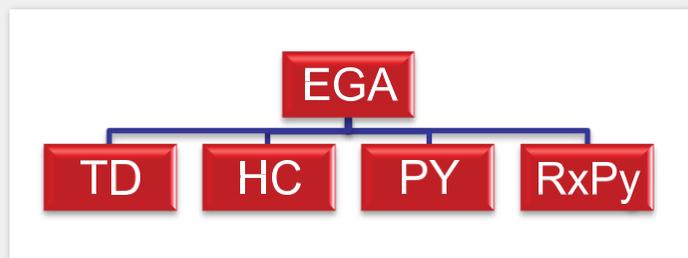


“Method Map” for Material Characterization

Frontier Lab has developed a sequence of tests referred to as the “method map” to chemically characterize samples using the EGA/PY-3030D Multi-Functional Pyrolyzer System in conjunction with a benchtop GC/MS. This sequence is applicable when characterizing virtually any organic material from volatiles to high molecular weight polymers.

The “**method map**” provides scientists with two simple steps for determining the organic composition of any unknown material:

- i. The first step is to perform an [Evolved Gas Analysis \(EGA\)](#). In this technique, the sample is dropped into the furnace which is at a relatively low temperature (ca. 40 - 100 °C). The furnace is then programmed to a much higher temperature (ca. 600 - 800 °C). Compounds “evolve” continuously from the sample as the temperature increases. A plot of detector response versus furnace temperature is obtained.



- ii. The second step is to use the EGA thermogram and selected ion chromatograms (EIC) to define the thermal zones of interest and then perform one or a combination of the following techniques:

Use the links below for more information.

[Thermal Desorption \(TD\)](#)

[Flash Pyrolysis \(Py\)](#)

[Heart Cutting \(HC\)](#)

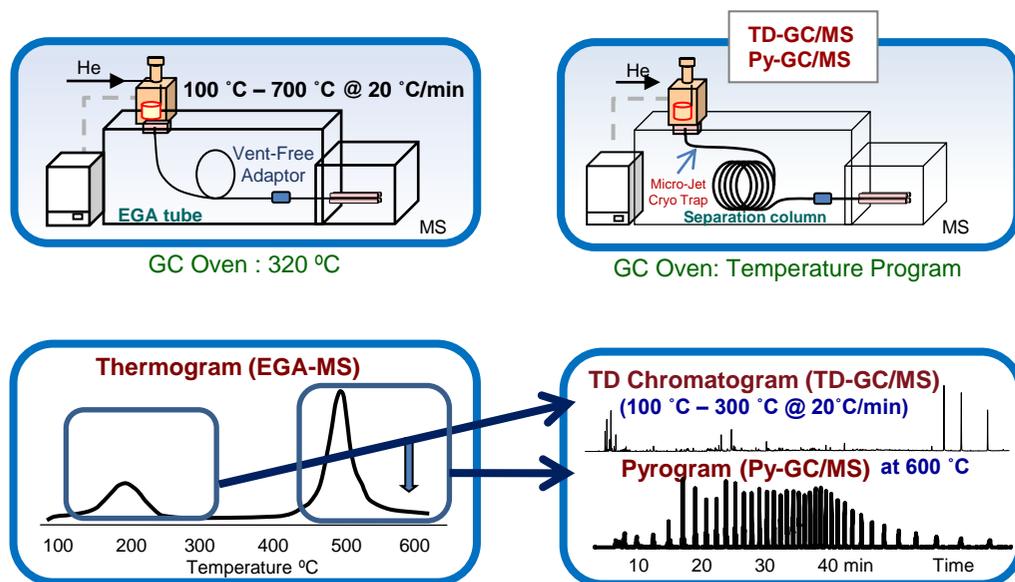
[Reactive Pyrolysis \(RxPy\)](#)

EGA & “Method Map”

EGA Configuration: No column is used; a short, small diameter (1.5m X 0.15mm id) deactivated tube connects the injection port to the detector. All thermal zones (interface temperature, GC injection port, column oven and detector cross-over) are held at elevated temperatures to prevent condensation. The figure below shows the EGA-MS configuration and a typical EGA thermogram.

Following EGA, the instrument is re-configured. The EGA tube is replaced by an analytical column. The Frontier [Vent-Free GC/MS Adaptor](#) enables this to be done easily and quickly; there is no need to vent the MS. MS vacuum equilibrium is re-established within a few minutes, and the exposure of the ion source to oxygen is minimized.

In this example, a double-shot analysis (TD of the thermally stable and the volatile components followed by Py of the residual sample in the cup) was performed to characterize the two thermal zones shown on the EGA thermogram. One sample is analyzed two times; the sequence is fully automated.



As shown in the Figure, information about the organic ‘volatiles’ in the sample is generated by simply introducing the sample at 300 °C, only the compounds evolving below 300 °C will evolve from the sample and be transported to the head of the column. If there is interest in both the volatile fraction and the higher boiling compounds, this can be done in two steps, and it may be necessary to add a micro-cryo trap. Thermal desorption is performed over time, e.g., 100 to 250 °C at 20 °C /min takes 7.5 minutes. The micro-cryo trap re-focuses the volatile analytes of interest at the head of the column so that the full separating power of the column can be utilized.

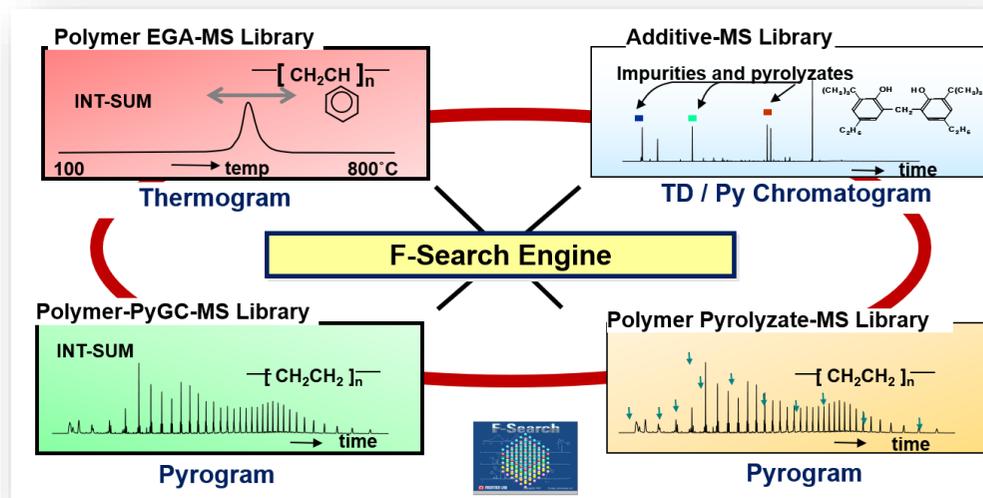
If there are more than two zones in the obtained EGA thermogram, Heart-cutting (HC) technique, which utilizes an accessory called a [Selective Sampler](#), slices the thermal zones out of the sample and separate the components chromatographically with detection by MS.

F-Search Engine

SIMPLIFYING AND IMPROVING THE ACCURACY OF DATA INTERPRETATION

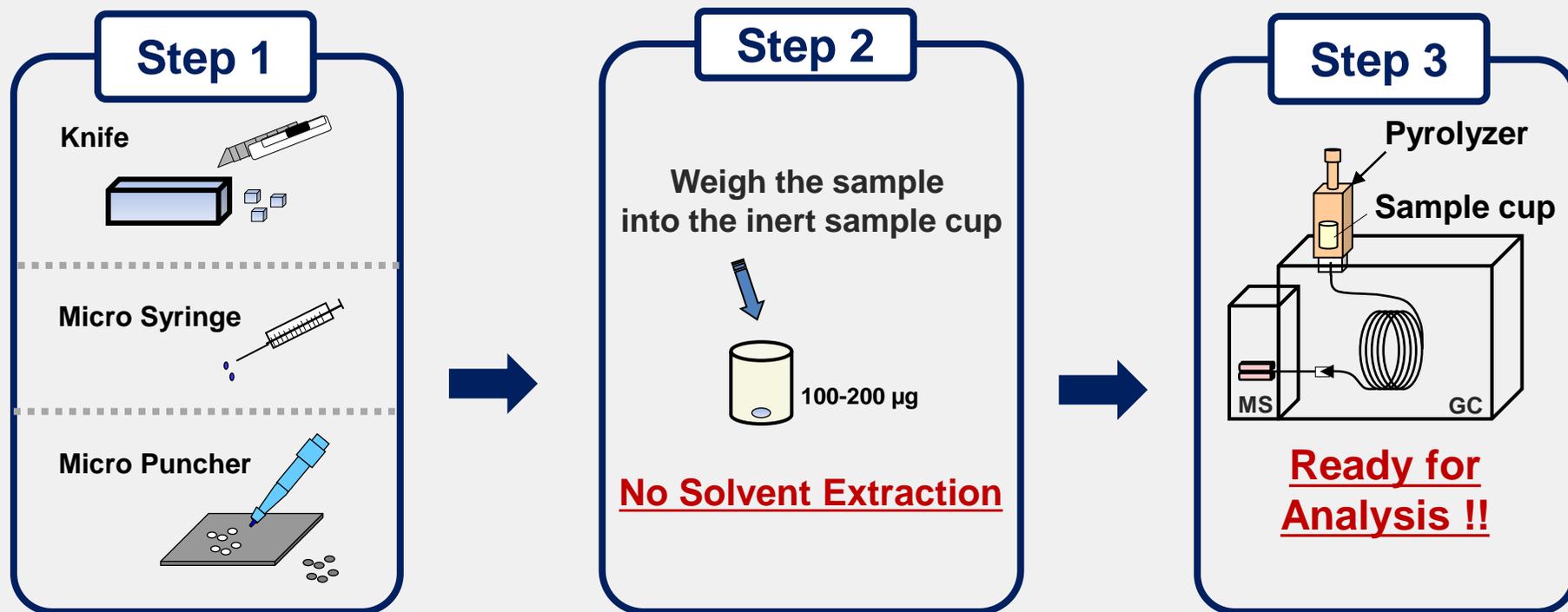
Polymeric materials often contain a variety of additives such as antioxidants, UV absorbers, etc. to assist during the production phase and determine the physical and chemical characteristics of the final product. These compounds are identified using commercial mass spectral (MS) libraries; however, these general-purpose MS libraries contain very few entries for pyrolyzates and additives which severely limits their utility for polymer characterization.

Frontier Laboratories developed a search engine and libraries called F-Search. The ions associated with hundreds of polymers, their degradation products (i.e., pyrolyzates) and hundred of additives are used to identify and thus characterize the sample as it is heated in the Py. The libraries include both chromatographic and mass spectral data. There are four unique libraries which allow users to select among them for specific purposes. The ability to create in-house specialty libraries is incorporated into the standard software. Updating these libraries is straightforward.

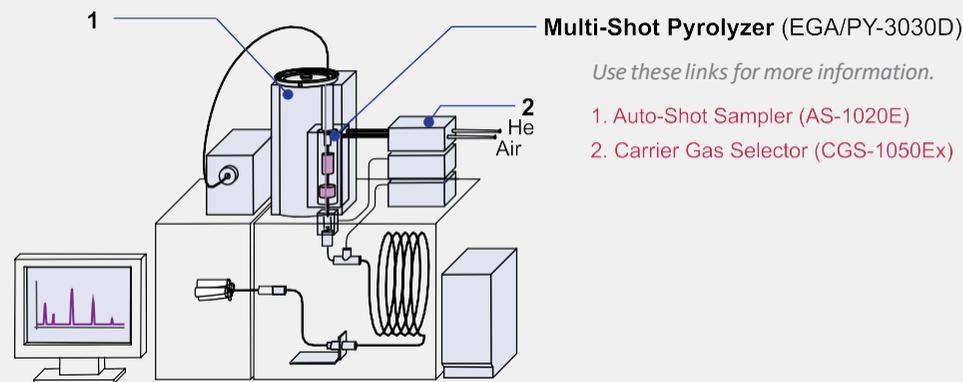


Easy Sample Preparation

This technology allows multiple analysis on a single sample. There is no need for solvent and sample preparation as the sample is simply introduced into the GCMS by the Frontier Pyrolyzer.



Pyrolysis-GC/MS System Configuration



1. Auto-Shot Sampler (AS-1020E)

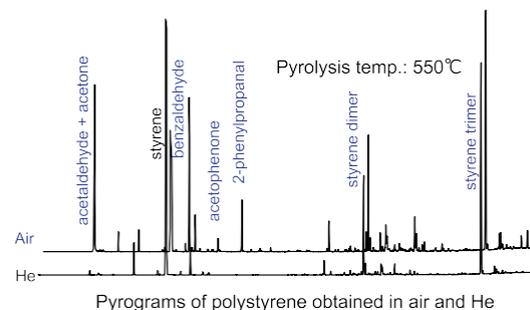
Up to 48 samples can be automatically analyzed using any of the analytical modes (e.g., TD, Py, Double-Shot, Heart-Cutting. Etc) with enhanced reliability.

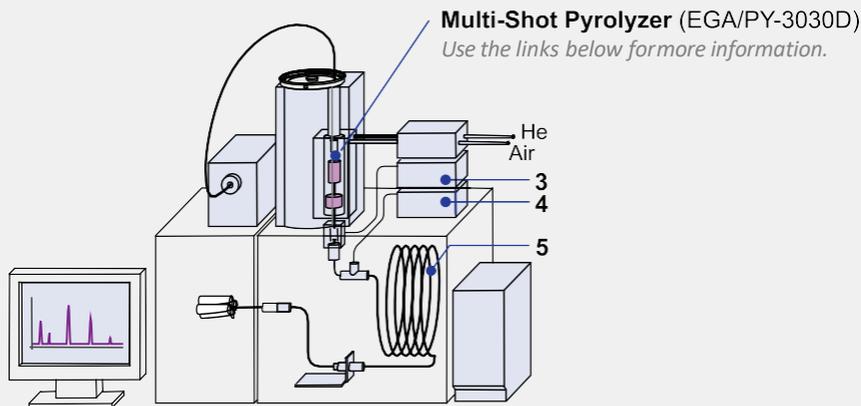


Pyrolyzer is located in the housing of Auto-Shot Sampler.

2. Carrier Gas Selector (CGS-1050Ex)

The device allows switching of the gas, e.g., He and air, surrounding the sample during analysis.



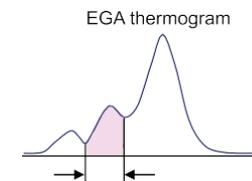


Multi-Shot Pyrolyzer (EGA/PY-3030D)
Use the links below for more information.

- 3. Selective Sampler (SS-1010E)
- 4. MicroJet Cryo-Trap (MJT-1035E)
- 5. Ultra ALLOY® metal capillary column

3. Selective Sampler (SS-1010E)

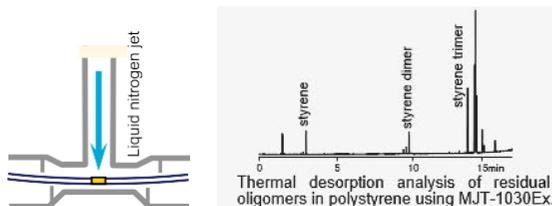
Any temperature zone as defined by the EGA thermogram, that is Heart-Cutting either manually or automatically, can be introduced to a separation column.



Any temperature zone can be heart-cut for GC/MS analysis.

4. MicroJet Cryo-Trap (MJT-1035E)

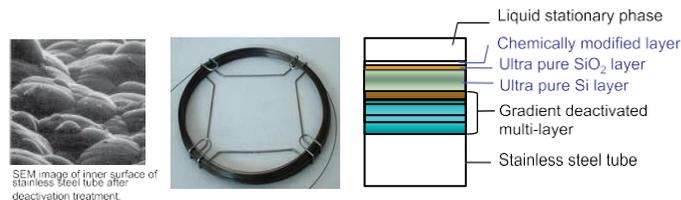
By blowing liquid nitrogen jet to the front of separation column, volatile compounds are cryo-trapped while maintaining the temperature at -196°C using only one third of the amount of liquid nitrogen required for competitors products. It supports automated analysis.



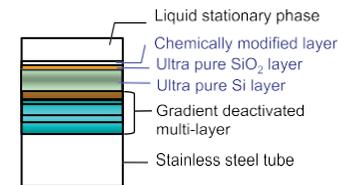
Thermal desorption analysis of residual oligomers in polystyrene using MJT-1030Ex.

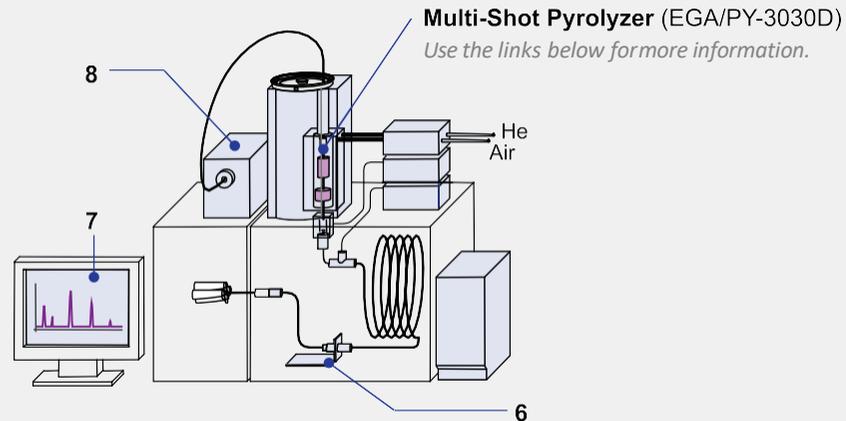
5. Ultra ALLOY® Metal Capillary Column

By multi-layer gradient deactivation treatment, these separation columns have high flexibility, high temperature, and contamination resistances.



SEM image of inner surface of stainless steel tube after deactivation treatment.

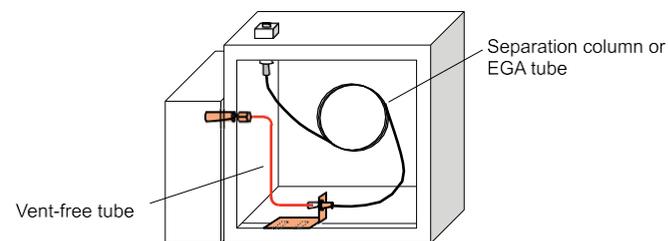




- 6. Vent-Free GC/MS adapter
- 7. F-Search system (search engine and libraries)
- 8. Micro UV irradiator (UV-1047Xe)

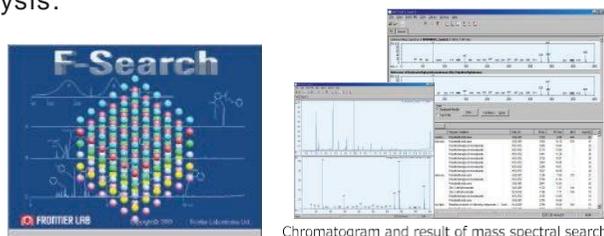
6. Vent-free GC/MS Adapter

Without venting MS, separation column and/or EGA tube can be switched.



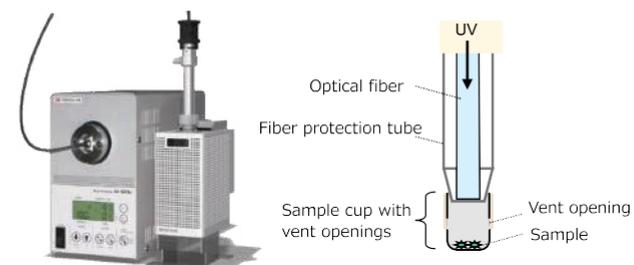
7. F-Search System (Libraries and Search Engine)

This software system supports identification of polymers and additives from data obtained by evolved gas analysis, thermal desorption, or pyrolysis GC/MS analysis.



8. Micro-UV Irradiator (UV-1047Xe)

With a strong Xe UV light source, photo, thermal, and oxidative degradation of polymers can rapidly be evaluated.



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- ELASTOMERS** NATURAL SYNTHETIC RUBBERS, SILICONES, SULFUR COMPOUNDS
- ENERGY**BIOMASS, OILS, COAL, HYDROCARBONS, GEOCHEMISTRY, BIOCHEMISTRY
- ENVIRONMENTAL**VOLATILES, POLLUTANTS, PESTICIDES
- FORENSIC AND SECURITY**..... FORENSIC EVIDENCES
- INKS AND PAINTS**PIGMENT, RESIN, SOLVENT, DEFOAMER, WAX, PHOTOCOPY TONER
- PAPER AND FIBERS** WOODS, PULP, COATINGS, SIZING AGENTS
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- OTHERS**MISCELLANEOUS APPLICATIONS



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