

# Solving Analytical Problems

Version 1.0

using Multi-functional Pyrolyzer®

## Application products

- Apparel
- Automobile
- Construction
- Cosmetics
- Food
- Packaging
- etc.



**FRONTIER LAB**

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## Introduction to Frontier Laboratories

In 1991, Frontier Laboratories introduced the first commercially available pyrolyzer based on a patented vertical micro-furnace. Since then, a number of innovative accessories have been developed which extend the capabilities of the system beyond simple pyrolysis. Today, the Frontier system can be configured to perform evolved gas analysis (EGA), multi-step thermal desorption and pyrolysis (TD/Py), reactive pyrolysis, and heart-cutting of individual EGA fractions...all automatically! A complete system enables the analyst to fully characterize virtually any complex sample.

The Frontier Multi-functional Pyrolyzer® is used to solve analytical problems – problems that occur in production, problems caused by product failure, problems with instrument contamination, problems with challenging sample preparation regimes, or problems that arise when faced with superior competitive products. These are just few of the areas which a Frontier Multi-functional Pyrolyzer® will prove to be the most cost effective means of responding to the everyday challenges encountered in the modern analytical laboratory.

This monograph presents several examples where the Frontier system is used to provide chemical characterization of a diverse set of sample matrices. In most instances, the “sample” is analyzed directly, which not only saves time but eliminates the inherent errors associated with conventional sample preparation techniques such as solvent extraction, derivatization, etc.

If you desire more information about any of the solutions presented or should you find yourself with a difficult analytical problem similar to these presented, your best source of information is the Frontier web site: [www.frontier-lab.com](http://www.frontier-lab.com).



All information subject to change without notice.

## Analytical problems and Frontier-Based Solutions

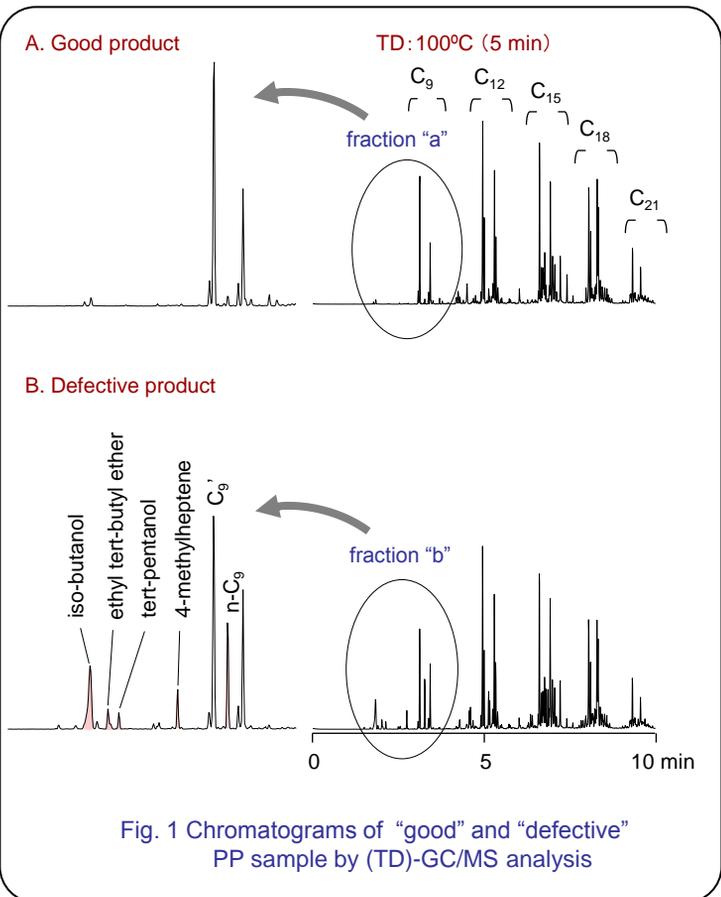
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**Problem:** What is the proper analytical method to detect odors emanating from polypropylene (PP) materials?

**Analysis:** About 7 mg of the PP sample is placed in the sampling cup and analyzed by TD- GC/MS.

**Result:** The (TD)-GC/MS chromatograms of “good” and “defective” PP are presented in Fig.1. The ‘defective’ sample contains a number of volatiles which are not present in the “good” sample. Therefore, it can be postulated that these additional volatiles may be responsible for the odors in the “defective” PP sample.





**Problem:** What is the first step to perform in the analysis of the unknown such as printer toner?

**Analysis:** EGA-MS method is one of the simple thermal analysis methods using a Double-Shot Pyrolyzer, and is the primary analysis method for unknown sample.

**Result:** Fig. 1 shows the thermogram of a printer toner and the average spectra of its temperature zones A, B, and C. Judging from the elution temperature, zones A and B are considered to be originated from evaporation and elimination of low molecular weight compounds. On the other hand, zone C is considered to be originated from a binder resin. Then, the average spectrum for zone C was searched using the EGA mass spectral library for polymers. Table 1 lists polymers that were hit by the library search. Styrenic and acrylic polymers are listed as candidates for the binder polymer. As described here, EGA-MS library search is a very powerful tool as the primary search method for the characterization of unknown polymeric materials.

Table 1 Results of EGA-MS library search on zone C

	Ref No.	Qual
1. Methyl methacrylate-butadiene-styrene copolymer	#165	90
2. Styrene-ethylene-butadiene-styrene-block copolymer	#195	86
3. Styrene-divinylbenzene copolymer	#210	80

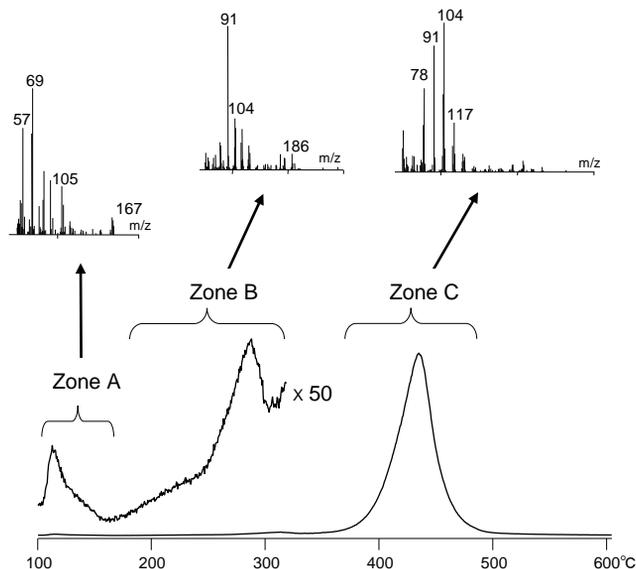


Fig. 1 EGA thermogram of a printer toner and mass spectra of three temperature zones

EGA capillary tube : 2.5M (id. 0.15mm), GC oven temperature : 300°C

**Problem:** A printer toner is composed of a binder resin, magnetic particles, colorant, and a mold-releasing agent, and was analyzed by evolved gas analysis (EGA) technique as shown in Fig. 1. What else can be done if a Double-Shot Pyrolyzer is used?

**Analysis:** Selective Sampler (SS-1010E) and MicroJet Cryo-Trap (MJT-1030E) allow components generated from each temperature zone to be introduced into a separation column and to be analyzed by GC/MS in detail.

**Result:** Fig. 2 shows GC/MS analytical results of Zones A, B, and C of the EGA thermogram shown in Fig. 1. Nitriles were found in Zone A, and in Zone B methyl methacrylate (MMA), styrene (S), styrene dimer (SS), styrene trimer (SSS) and other aromatic compounds (marked with •) were found. Also, in Zone C the pyrolyzates of methyl methacrylate-butadiene-styrene copolymer were detected as a binder resin component.

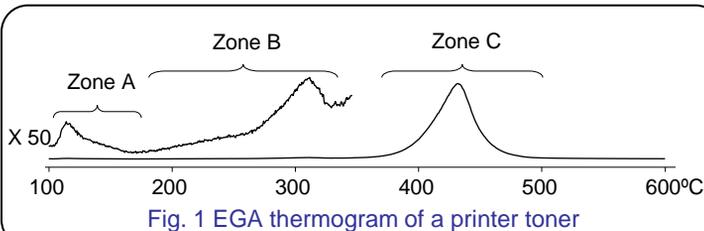


Fig. 1 EGA thermogram of a printer toner

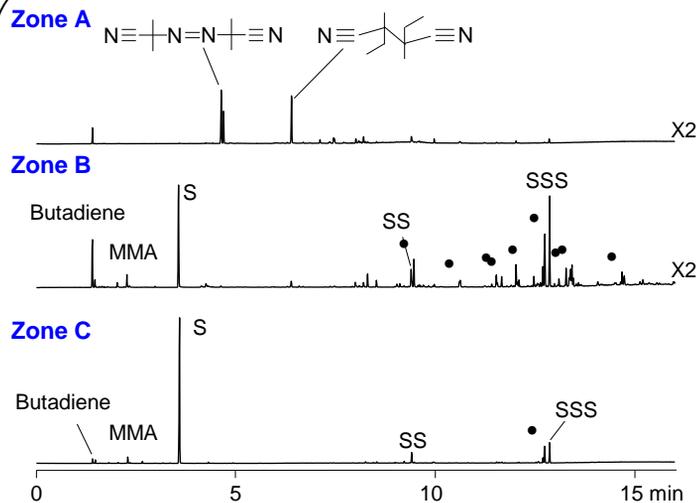


Fig. 2 Chromatogram of each temperature zone of EGA profile

Separation column : Ultra ALLOY+5 30M-0.25F

GC oven temperature : 40°C~20°C/min~320°C (2min hold)

**Problem:** Is there an easy way to analyze hazardous compounds out-gassing from food wrap film?

**Analysis:** A piece of polyvinylidene chloride film (0.25 cm<sup>2</sup>, 0.5 mg) is placed in the sample cup and analyzed by EGA-MS and Heart-Cut EGA-GC/MS method.

**Result:** The EGA thermogram of the film is presented in Fig. 1. Each zone is analyzed separately using a Heart-Cut EGA-GC/MS technique. The results of the analyses are shown in Fig. 2. The data indicates that a number of additives and pyrolyzates of the polymer back bone are present in each EGA zone.

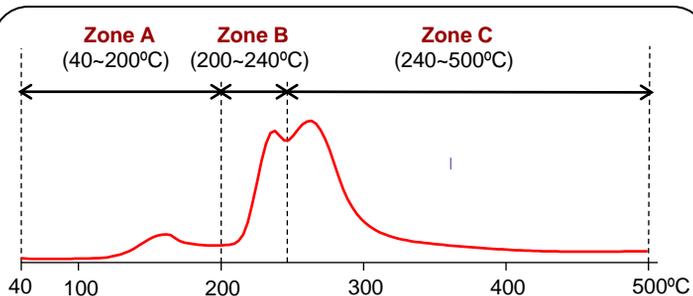


Fig.1 Thermogram of food wrap film

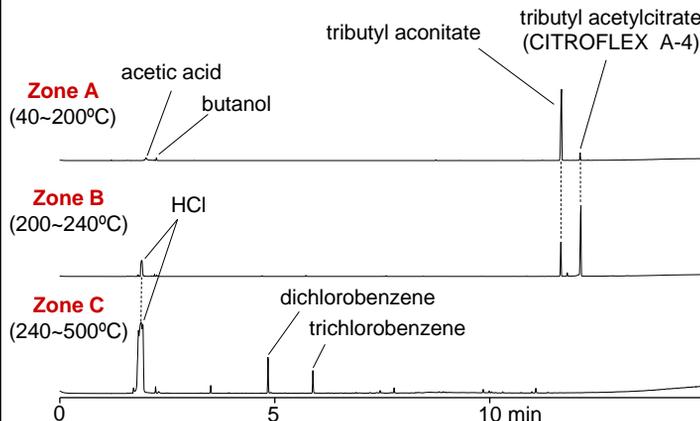


Fig. 2 Chromatograms for Zones A through C by Heart-Cut EGA-GC/MS method

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

**Analysis:** The analysis can be performed using a Double-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 (MJT-1030E)

**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 C<sub>6</sub>, C<sub>9</sub>, C<sub>12</sub>, and C<sub>15</sub> derived from pyrolysis of polypropylene, and ε-caprolactam, monomer of nylon-6, were observed.

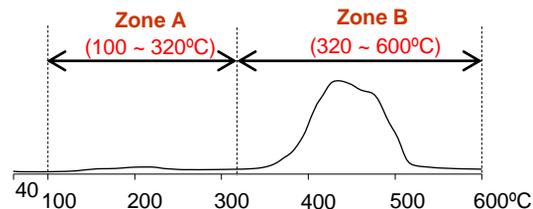


Fig. 1 EGA Profile of Polypropylene + Nylon

Pyrolysis temp: 40–600°C (30°C/min), carrier gas: He,  
Deactivated metal capillary column (length: 2.5m, id: 0.15mm)

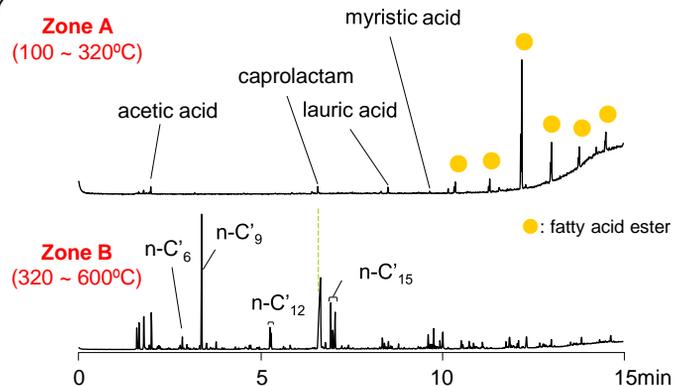


Fig. 2 Analysis Results of Zones A and B of Polypropylene + Nylon

Separation column: Ultra ALLOY-5, 30M-0.25F,  
GC oven temp: 40°C (1min hold) ~ 320°C (20°C/min)

**Problem:** Can a crude drug propolis harvested from two different areas be differentiated by Py-GC/MS Analysis?

**Analysis:** Flash pyrolysis (Py)-GC/MS technique was used to obtain pyrograms of two propolis samples obtained from different areas, and the compositions were compared.

**Result:** Fig. 1 shows pyrograms of two different samples of propolis. Phenols, aromatic acids, sesquiterpenes, ethyl esters of C<sub>16</sub>-C<sub>18</sub> aliphatic acids, and various flavonoids were observed in the pyrograms. The peak distributions for aromatic acids and phenols derived from these two kinds of propolis showed a similarity, while the peak distributions for ethyl esters of C<sub>16</sub>-C<sub>18</sub> aliphatic acids and flavonoids showed a large difference.

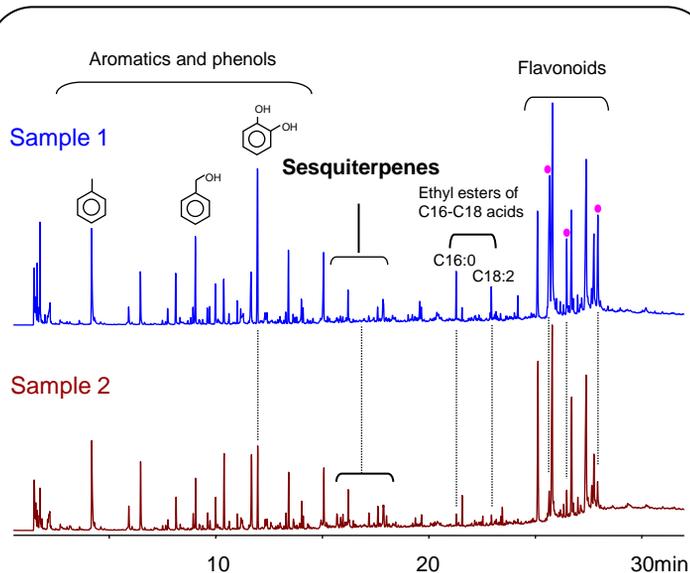


Fig. 1 TIC pyrograms of two different propolis samples

Double-Shot Pyrolyzer: PY-2020ID

Pyrolysis temperature: 550°C, Column head pressure: 50kPa, Split ratio: 1/50

Separation column: Ultra ALLOY+5(5% diphenyl 95% dimethylpolysiloxane),

L=30 m, id=0.25 mm, DF=0.25 μm, GC oven: 40°C~300°C (10°C/min), Sample:

300 μg, Detector: MS (m/z: 29-550, 2 scans/sec)

**Problem:** Can analysis using Double-Shot Pyrolyzer differentiate the components of crude drug propolis harvested in different areas?

**Analysis:** They can be differentiated using evolved gas analysis (EGA) method followed by analysis of the volatile temperature zone of the EGA thermogram. The volatile fraction zone is introduced into a separation column and is analyzed by Heart-Cut EGA-GC/MS technique.

**Result:** Fig. 1 shows EGA thermograms for two types of propolis. The zone A was each analyzed by Heart-Cut EGA-GC/MS method. The chromatograms for both are shown in Fig. 2. Comparison of sample 1 with sample 2 reveals that essential oils and volatile flavonoid regions were significantly different.

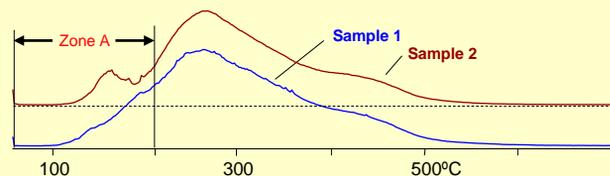


Fig. 1 EGA thermograms of different propolis

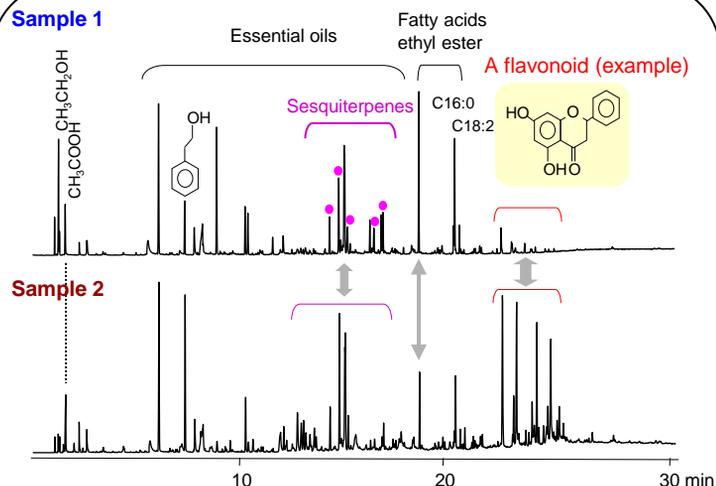


Fig. 2 Chromatograms of 2 types of propolis obtained from Zone A

Separation column : Ultra ALLOY+-5 30M-0.25F  
GC oven temperature : 40°C~10°C/min~300°C (5min)

**Problem:** How can photodegradative changes in the chemical structures of silk be analyzed?

**Analysis:** Photodegradation of silk samples was performed by exposure to simulated sunlight of a weather-meter at 46°C with 60±5% relative humidity for 52 days. About 200 µg of silk sample was pyrolyzed at 600°C under He atmosphere and selectively detected by a sulfur chemiluminescence detector (SCD).

**Result:** As shown in Fig. 1, the intensities of the key peaks apparently decreased upon exposure to light. The contents of Met, Cys, and Cys-Cys residues in the silk samples were then determined from the corresponding key peak intensities using calibration curves. The quantitative results thus obtained for the silk samples are summarized in Table 1. The RSD for the Cys residue determination was ca. 5% in three repeated runs for the control sample.

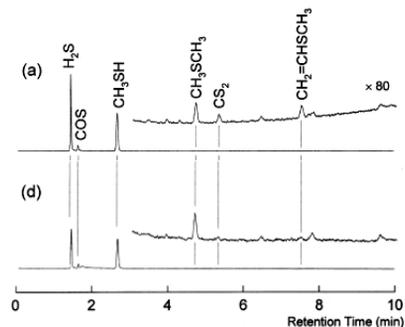


Fig. 1 Pyrograms of photo degraded silk samples at 600°C observed by SCD: (a) not exposed and (b) exposed for 52 days

Table 1 Sulfur-containing amino acid residues in exposed silk samples determined by Py-GC with SCD

Sulfur containing Amino acid	Amino acid residue [mmol/g] Amino acid composition [wt%]	
	No exposure	52-day exposure
Met <sup>a*</sup>	14.8±2.9 (0.22)	10.6±2.0 (0.16)
Cys <sup>b*</sup>	14.6±0.8 (0.18)	7.0±0.2 (0.08)
Cys-Cys <sup>c*</sup>	1.48±0.19 (0.036)	0.54±0.23 (0.013)

<sup>a\*</sup> from peak intensity of CH<sub>3</sub>SH

<sup>b\*</sup> from peak intensity of H<sub>2</sub>S

<sup>c\*</sup> from peak intensity of CS<sub>2</sub>

**Problem:** How can the brominated flame retardant DeBDE (decabromodiphenyl ether) in waste plastics be analyzed qualitatively and quantitatively?

**Analysis:** A sample containing DeBDE is placed in a sample cup, and is analyzed by EGA-MS and thermal desorption (TD)-GC/MS techniques.

**Result:** The results obtained by EGA-MS technique is shown in Fig. 1. The major peak observed at 400~500°C was found to be a polystyrene by F-Search with polymer library. The average mass spectrum for the weak peak observed at 250~350°C contained m/z 799 and molecular ion m/z 959, both of which are characteristic to DeBDE. The mass chromatogram drawn with m/z 959 clearly showed the elution profile for DeBDE. From this result, thermal desorption temperature for DeBDE was determined to be 200~400°C (20°C/min). Fig. 2 shows the result of DeBDE determination obtained by (TD)-GC/MS using this condition. As clearly indicated, DeBDE was detected without any interference from coexisting materials, and RDS (reproducibility) of 3.5% was obtained with the DeBDE content found to be 7.1wt%.

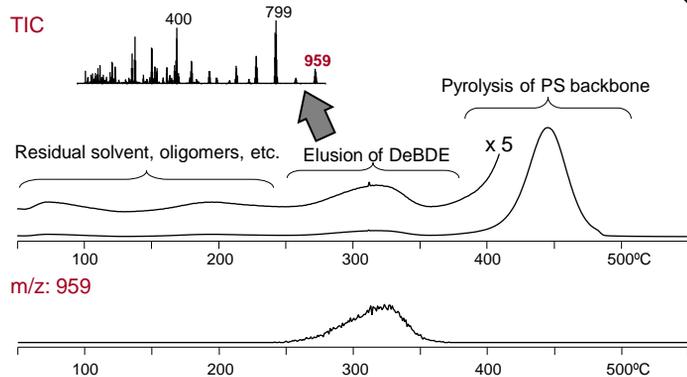


Fig. 1 EGA thermogram of waste plastic

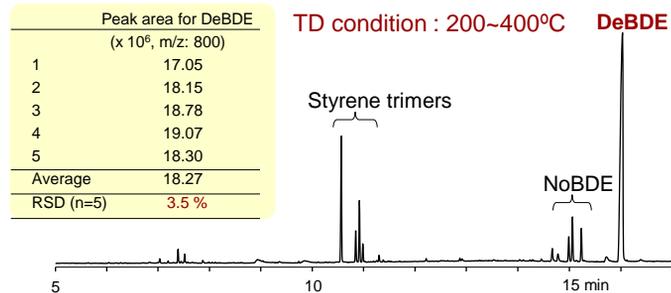


Fig. 2 Chromatogram of waste plastic obtained by (TD)-GC/MS

Separation column : UA-PBDE 15M-0.05F

Thermal desorption temp. : 200°C~20°C/min - 400°C

**Problem:** How can additives in recycled polypropylene be analyzed? How are they identified?

**Analysis:** The MS library for additives, ADD-MS06 Library, contains pyrograms for the standard additive samples obtained by Py-GC/MS at 600°C, mass spectra for the major peaks observed on each pyrogram, retention indices (RI) of the major peaks of the additive, and pyrolyzates. Using this library, additives of a recycled polypropylene (PP) were identified from its chromatogram obtained by thermal desorption GC/MS analysis.

**Result:** Fig. 1(a) shows the observed TIC for the recycled PP obtained by (TD)-GC/MS. The search results for the mass spectra of peaks A and B are shown in Table 1. The both peaks were identified by narrowing down the candidates by match quality and RI comparison. Pyrograms of additives stored in the ADD-MS06 Library are shown in Figs. 1(b), (c), and (d). Comparing these, additives contained in the recycled PP can be identified as an antioxidant for the peak A and a flame retardant for the peak B.

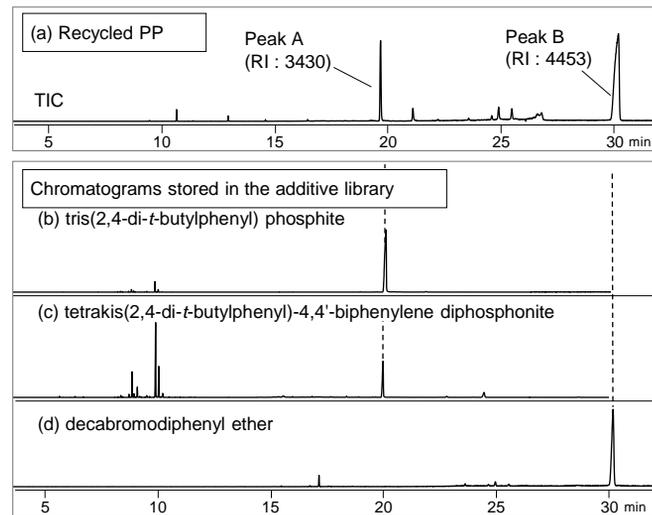


Fig. 1 Chromatograms of PP, and additives stored in MS library

TD: 100 - 300°C(20°C/min), GC Oven: 40 - 320°C(20°C/min, 4 min) - 340°C(10°C/min), He: 1.0 ml/min, Split ratio: 1/50, Amount: 0.3 mg, Col : UA5-30M-0.25F

Table 1 Additive MS library search results

	Candidates compounds	Match quality[%]	RI
Peak A RI:3430	1. <b>tris(2,4-di-t-butylphenyl) phosphite</b>	<b>62</b>	<b>3451</b>
	2. 2,4,8,10-tetra-t-butyl-5,7-dioxo-6-phospha-dibenzo[a,c]cyclohepten-6-ol	55	2888
	3. 2-t-butyl-6-methyl-4-ethenylphenol	1	1535
Peak B RI:4453	1. <b>decabromodiphenyl ether</b>	<b>89</b>	<b>4412</b>
	2. isomer of bromophenyl heptabromodiphenyl ether	13	3738
	3. tetrabromo phthalimide	5	2814

**Problem:** When flash pyrolysis is used for the analysis of additives in a polymer, interferences caused by the pyrolyzates of the polymer backbone often leads to poor analytical precision. How do you get the thermal property of such additives?

**Analysis:** The quantitative analysis of butylhydroxy-toluene (BHT, Fig. 1), an additive commonly used as antioxidant for PE, using (TD)-GC/MS is illustrated here. First, evolved gas analysis (EGA) was performed in temperature range 100–600°C to determined the thermal property of the sample.

**Result:** The thermogram of the PE sample, obtained by EGA, is shown in Fig. 2. In the TIC chromatogram, only a single peak, emanating from the pyrolysis of PE, is observed. Extracted ion chromatograms:  $m/z$  205 and 220 which are characteristic ions for BHT, are observed in the temperature range 100–200°C. This defines the thermal desorption conditions (100–200°C at 20°C/min, 3 min hold) for determining BHT in PE.

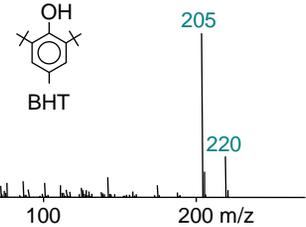


Fig. 1 Chemical structure of BHT and its mass spectrum

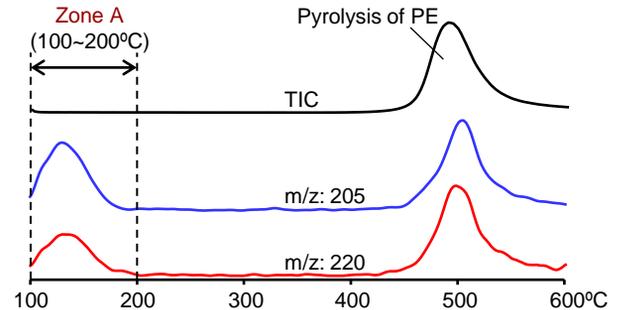


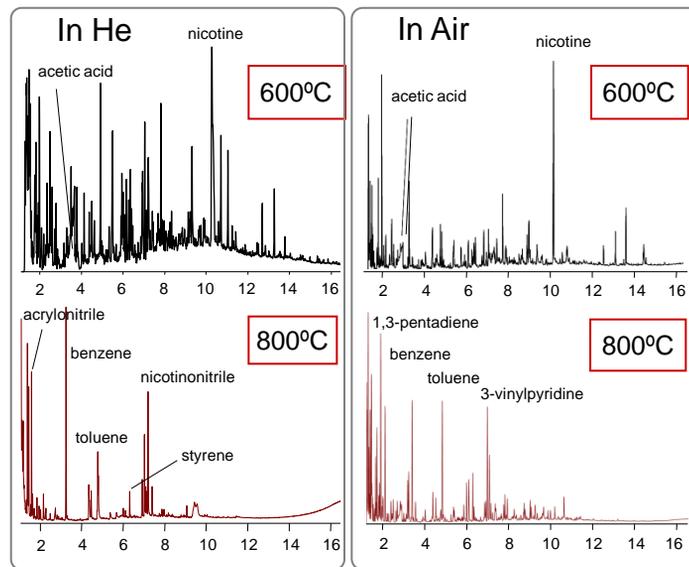
Fig. 2 Thermograms of a PE Sample

Pyrolyzer furnace temp. : 100–600°C, (20°C/min),  
Split ratio : 1/50, sample size : about 0.5mg, detector : MS

**Problem:** Temperatures reached during the burning of tobacco often exceed 700°C. Are there any examples in which the pyrolysis of tobacco was performed in air and in Helium using pyrolysis-GC/MS?

**Analysis:** Pyrograms were obtained in air and He at 600 and 800°C using Py-GC/MS.

**Result:** There are significant differences between the left (He) and right (air) pyrograms. Nicotine found in He at 600°C is thermally decomposed to nicotinonitrile, and the peak for acetic acid is greatly reduced at 800°C. In an oxidative atmosphere, nicotine is degraded to 3-vinylpyridine and the formation of benzene is evident at 800°C. The comparison of pyrolyzates formed in He and in oxidative atmosphere provides you with a good insight into the decomposition process.



**Fig. 1** Pyrograms of tobacco obtained at 600°C and 800°C under air and helium atmosphere

Separation column: Ultra ALLOY-1 30M-0.5F  
GC oven: 40 (2 min)-320°C (20°C/min)

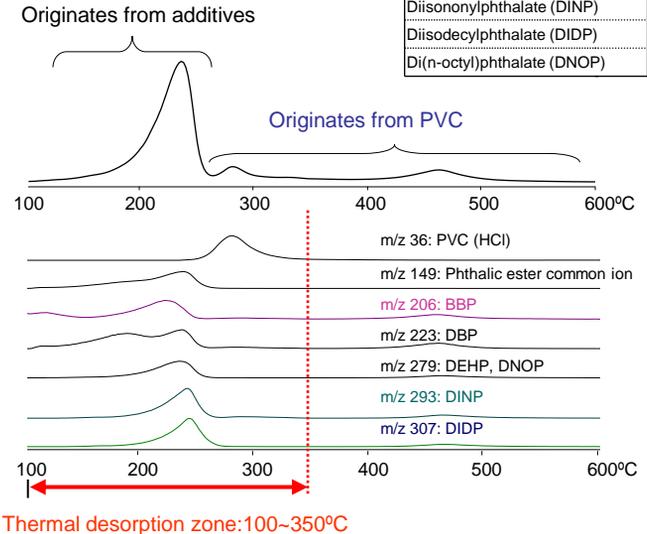
**Problem:** How can the thermal desorption temperature zone for restricted phthalates shown in Table 1 be determined?

**Analysis:** The thermal desorption temperature zone is determined by evolved gas analysis (EGA-MS). In this example, commercial polyvinyl chloride (PVC) toy sample, to which 1% each of six different phthalates (Table 1) was added, was analyzed by EGA.

**Result:** Thermogram obtained by EGA-MS is shown in Fig. 1. Peaks originated from both additives and PVC were observed. From the characteristic mass fragmentogram for the six restricted phthalates, the temperature range in which all phthalates were thermally desorbed was determined to be 100 to 350°C.

**Table 1. Use restricted phthalates**  
(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** TIC thermogram and extracted mass chromatograms of PVC, to which 1% each of phthalate was added

Pyrolyzer furnace temp.: 100 – 600°C (20°C/min)  
EGA tube: UADTM-2.5N

**Problem:** The quantitative analysis of volatile additives in polymers is adversely effected by additive losses leading to decrease in analytical precision. Is there any way to get around this problem?

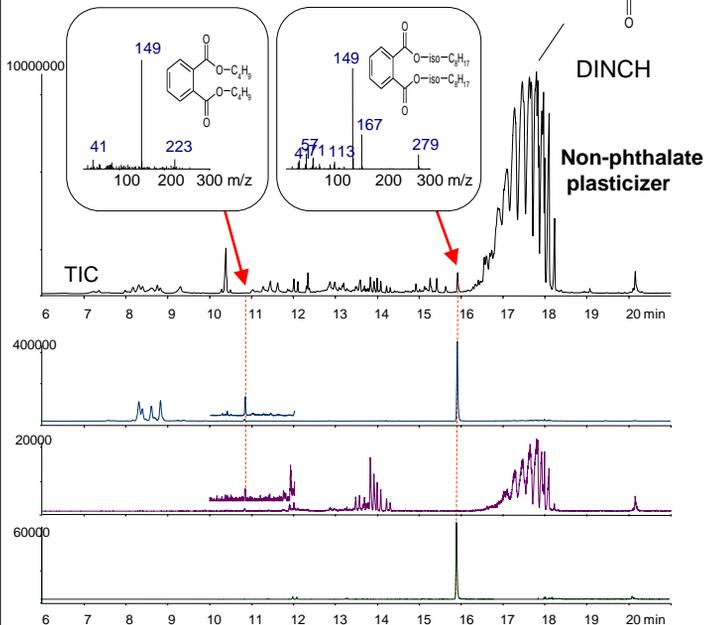
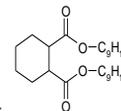
**Analysis:** Solid samples were milled to 45 mesh, and thin films were prepared by solvent casting, and were analyzed by (TD)-GC/MS. The thermal desorption zone for the phthalates was determined to be 100-350°C. The levels of the phthalates were calculated using an absolute area calibration

**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 minute 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 ppm 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.

**DBP (dibutyl phthalate) DEHP (di-2-ethylhexyl phthalate)**

**Ca. 50 ppm**

**ca. 300 ppm**



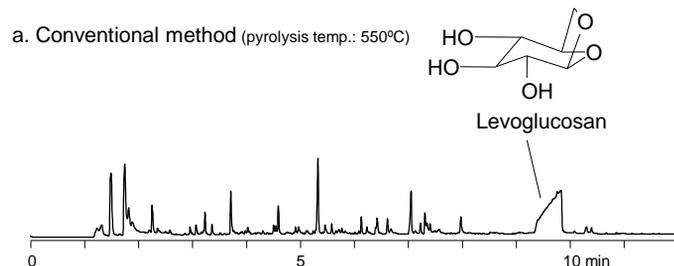
**Fig. 1** TIC and extracted ion chromatograms of a PVC sample obtained by (TD)-GC/MS

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<sup>+</sup>-1 30M-0.25F

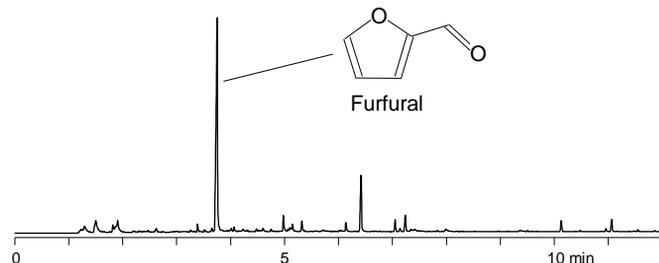
**Problem:** The reproducibility of quantitative analysis of cellulose pyrolyzates which contains levoglucosan as the major component and is used as an index is poor. Is there a better way to do this?

**Analysis:** 5  $\mu\text{L}$  of aqueous solution of cobalt sulfate (140 g/L) is added to 0.2 g of a sample, then allows it to dry. The dried sample is then subjected to reactive pyrolysis.

**Result:** Fig.1a shows a pyrogram obtained by the conventional Py-GC technique. Since pyrolyzates from cellulose showed up as more than 50 peaks with levoglucosan as the major component, the relative standard deviation (RSD) of quantitated results was as bad as 30%. Now aqueous solution of cobalt sulfate was added, then the dried sample was analyzed by reactive pyrolysis. A simplified pyrogram with furfural as the major component was obtained as shown in Fig.1b. Quantitative analysis was performed using the peak area of furfural. The reproducibility as expressed in RSD value was as good as 2.7%. This result shows that reactive pyrolysis of cellulose in the presence of  $\text{CoSO}_4$  enables quantitative determination of cellulose contained in a sample.



b. Reactive pyrolysis in presence of  $\text{CoSO}_4$  (pyrolysis temp.: 550°C)



**Fig. 1** Simplifying cellulose pyrogram by use of  $\text{CoSO}_4$

Separation column : Ultra ALLOY<sup>+</sup>-5 30M-0.5F

GC oven temp. : 40°C - 20°C/min - 320°C (2min)

**Problem:** Is there a simple way to perform compositional analysis of polyunsaturated fatty acid (PUFA) oils?

**Analysis:** One-step thermally assisted hydrolysis and methylation (THM)-GC in the presence of trimethyl sulfonium hydroxide (TMSH) is a simple way to determine fatty acid components especially of PUFA in lipid samples. One such example is described here.

**Result:** Fig. 1 shows typical chromatograms of a soybean oil obtained by one-step THM-GC in the presence of (a) TMSH and (b) TMAH. Many isomer peaks for C18:2 and C18:3 resulted from the thermal isomerization in the presence of TMAH are observed. On the other hand, these isomers are hardly seen in the case of (b) TMSH. Table 1 summarizes the chemical compositions of fatty acids in the soybean oil obtained by the one-step THM-GC in the presence of both TMSH and TMAH, together with those obtained by the offline transmethylation. The fatty acid compositions obtained using 0.2M of TMSH were in good agreement with those obtained by the offline GC method.

Fig. 1 Chromatogram of soybean oil obtained by one-step THM-GC at 350°C

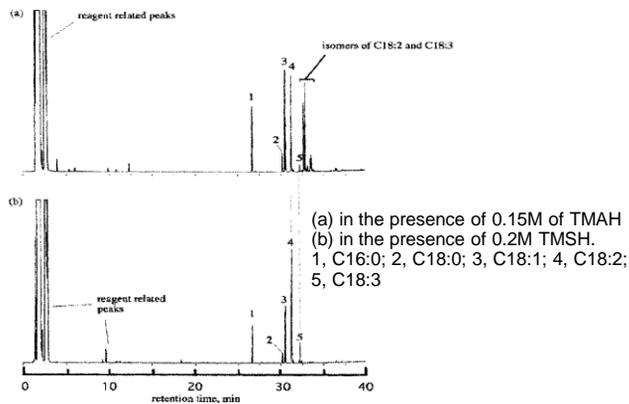


Table 1 Chemical composition and recovery of fatty acid components in soybean oil obtained by one-step THM-GC

	Fatty acid					
	16:0	18:0	18:1	18:2	18:3	Isomers of Total 18:2&18:3
Offline method*	13.2	4.0	22.6	54.6	5.7	nd 100
One step THM-GC						
THSH 0.2M	13.4(74.6)	3.7(76.5)	22.8(81.5)	54.8(80.6)	5.4(75.5)	nd 100
TMAH 0.05M	13.4(18.2)	3.6(17.3)	22.1(21.0)	55.2(19.2)	5.7(18.2)	nd 100
0.1M	13.2(43.6)	3.7(42.2)	22.4(51.5)	48.2(37.7)	5.1(36.5)	7.4 100
0.15M	13.3(83.5)	3.9(82.5)	23.2(99.6)	22.5(40.5)	1.1(22.1)	34.8 100

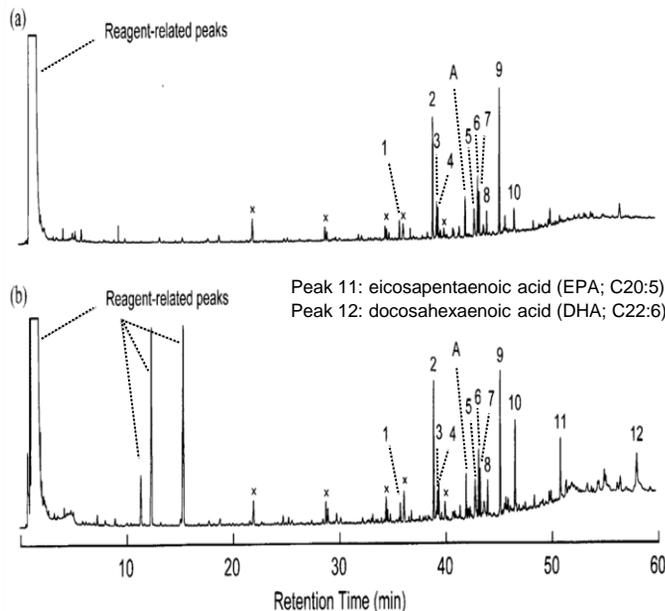
\*Offline transmethylation by TMSH followed by GC measurement

Data in parenthesis: recovery obtained from the observed molar peak intensity normalized by sample weight.

**Problem:** Can bio-samples such as lipids in water fleas be analyzed?

**Analysis:** Lipids in water fleas can be analyzed by reactive pyrolysis. Tetramethylammonium hydroxide (TMAH) is a commonly used reagent. Here, methylation using TMAH and trimethyl-sulfonium hydroxide (TMSH) is performed and results are compared.

**Result:** Fig. 1 shows pyrograms of water fleas sample obtained by reactive pyrolysis at 400°C in the presence of (a) TMAH and (b) TMSH. In each pyrogram, saturated and unsaturated fatty acids with carbon number 14 to 18 of water flea's constituent fatty acids are observed as methyl esters. EPA (peak 11) and DHA (peak 12) having 5 and 6 double-bonds, respectively, were methyl-derivatized using TMSH. Corresponding methyl derivatives were observed; however, almost no methylated products were observed in chromatogram (a) obtained using TMAH. This result shows that by using TMSH a series of fatty acids including thermally unstable unsaturated fatty acids could be detected at high sensitivities without any discernible side reactions.



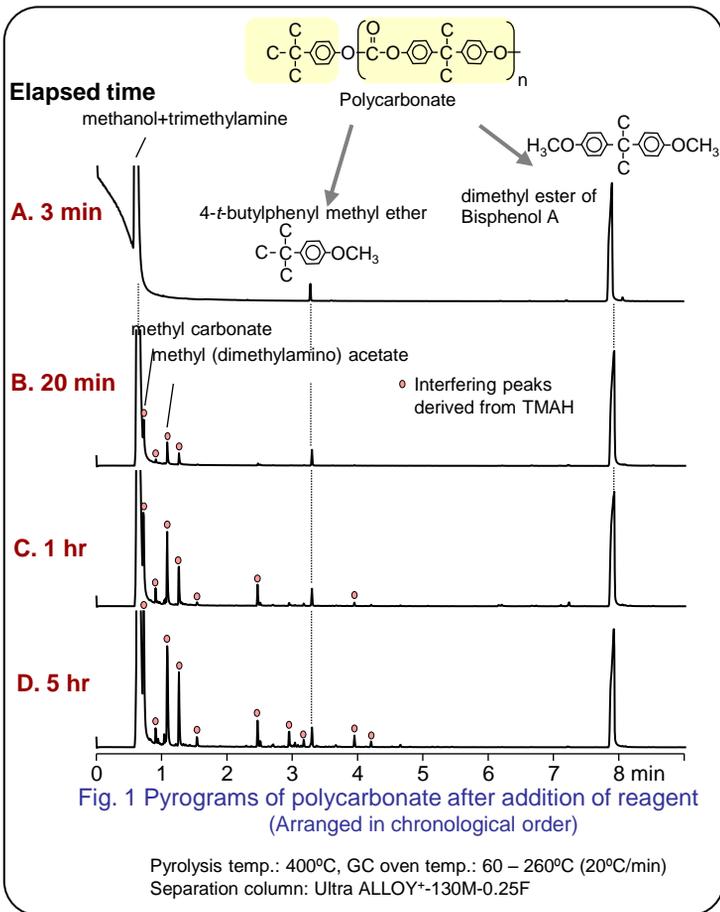
**Fig. 1** Analysis of lipids in water fleas using reactive Py-GC (a) in presence of TMAH, (b) in presence of TMSH

Separation column : Ultra ALLOY-CW, 30M-0.25F  
GC oven temperature : 50°C~5°C/min~240°C

**Problem:** Reactive Py-GC in the presence of a strong alkali such as tetramethyl ammonium hydroxide (TMAH), is used for the precise characterization of condensation polymers and fatty acids. Does the time interval between adding the reagent and the actual analysis effect the analytical results?

**Analysis:** 9  $\mu\text{g}$  of polycarbonate (PC) was placed in a sample cup, followed by addition of 3  $\mu\text{L}$  of a methanolic solution of TMAH (25wt%). Reactive Py-GC/MS was performed at 400°C at different time intervals.

**Result:** Fig. 1 shows pyrograms obtained at different time intervals after the addition of TMAH. Pyrogram A had a peak for the dimethyl ester of bisphenol A and the methyl ester of 4-*t*-butylphenol, which originates from the terminal group. As the time interval increases, the peak intensities and the ratio for the two peaks originating from PC remained unchanged; however, peaks for amines and methyl esters not observed in pyrogram A and not derived from PC were observed. These results show that when using TMAH, the analysis should be started as soon as possible.



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