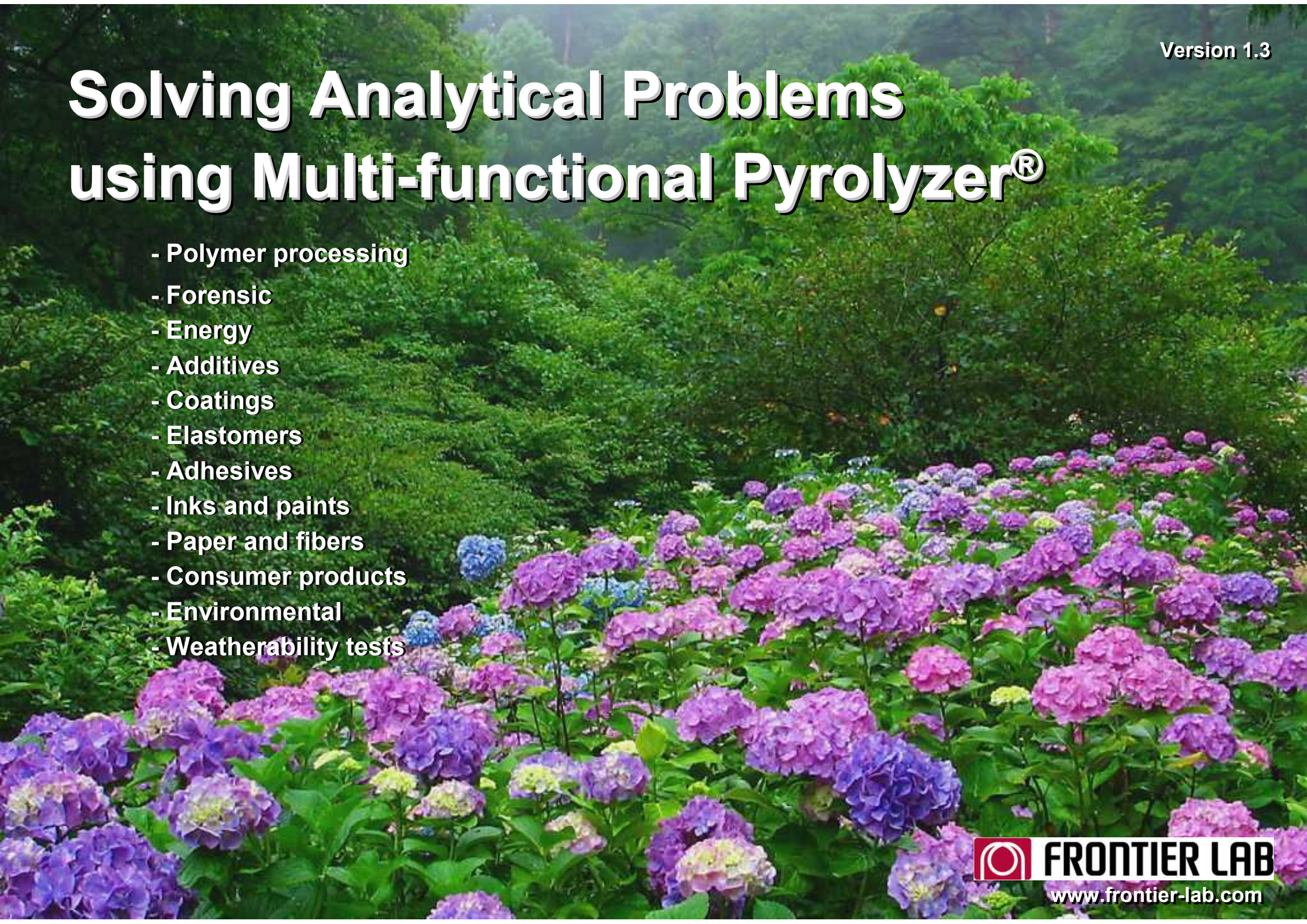
Version 1.3

Solving Analytical Problems using Multi-functional Pyrolyzer®

- Polymer processing
- Forensic
- Energy
- Additives
- Coatings
- Elastomers
- Adhesives
- Inks and paints
- Paper and fibers
- Consumer products
- Environmental
- Weatherability tests



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Analytical Problems and Frontier-Based Solutions - continues to next page

A. Polymer processing

B. Forensic

C. Energy

D. Additives

E. Coatings

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A-1

Problem: Is there a way to characterize polymerization reagents incorporated into poly(methyl methacrylate) chains by Py-GC?

Analysis: PMMA samples were prepared both with and without polymerization reagents. A pyrolyzer was attached to a GC with an FID or a flame photometric detector (FPD). Identification of peaks on the pyrograms was done using a GC-MS with both EI and CI sources.

Result: Figure 1 shows the pyrograms of samples prepared both (a) in the presence and (b) in the absence of polymerization reagents at 460°C. Since PMMA tends to depolymerize mostly into the original monomer at elevated temperatures around 500°C, the main pyrolysis product on the pyrograms (>90%) was the MMA monomer. As noted, peaks A through I are not observed on the pyrogram (b). Therefore, they can be assigned to the fragments of the polymerization reagents incorporated into the polymer chain.

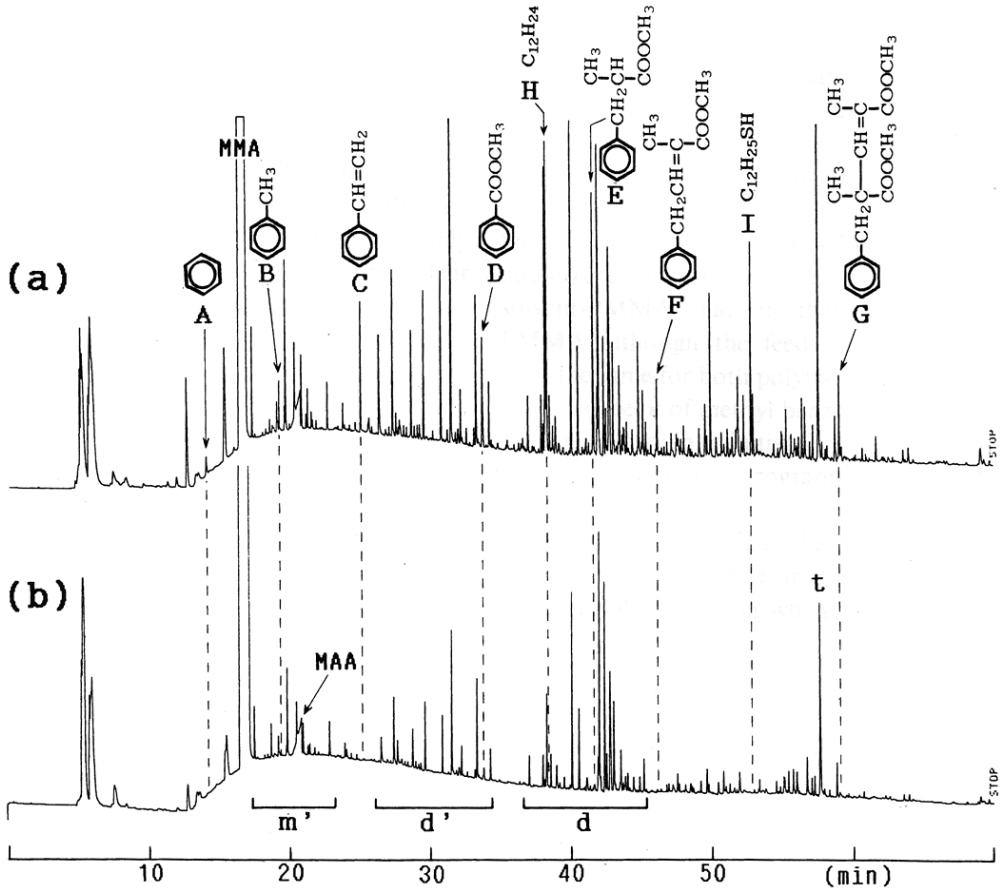

Fig. 1. Pyrograms of poly(methyl methacrylate):

(a) prepared in toluene with 0.3% of benzoyl peroxide and 1.5% of dodecanethiol; and
(b) thermally polymerized in bulk without any polymerization reagent.

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-036E

A-2

Problem: Has the end groups in radically polymerized poly(methyl methacrylate) been studied by Pyrolysis-GC?

Analysis: PyGC technique was used to characterize the end groups of PMMA samples which had been radically polymerized in toluene with BPO. 0.5mg of the polymer sample was pyrolyzed at 460°C under nitrogen.

Result: Fig. 1 shows the pyrograms of PMMA samples polymerized with 0.3% of BPO as the initiator in toluene, in benzene, and thermally polymerized without any reagents, respectively. Generally, the main pyrolysis product (>95%) is the MMA monomer formed. Among these, several peaks (A through G) on the pyrogram (a) are identified as the products having a phenyl ring, all of which are scarcely observed on the pyrogram (c). Also, peaks B (toluene), C (styrene) and F are exclusively observed in (a). Therefore, these three products should be derived mainly from the solvent fragments incorporated into the chain ends through the chain transfer to toluene.

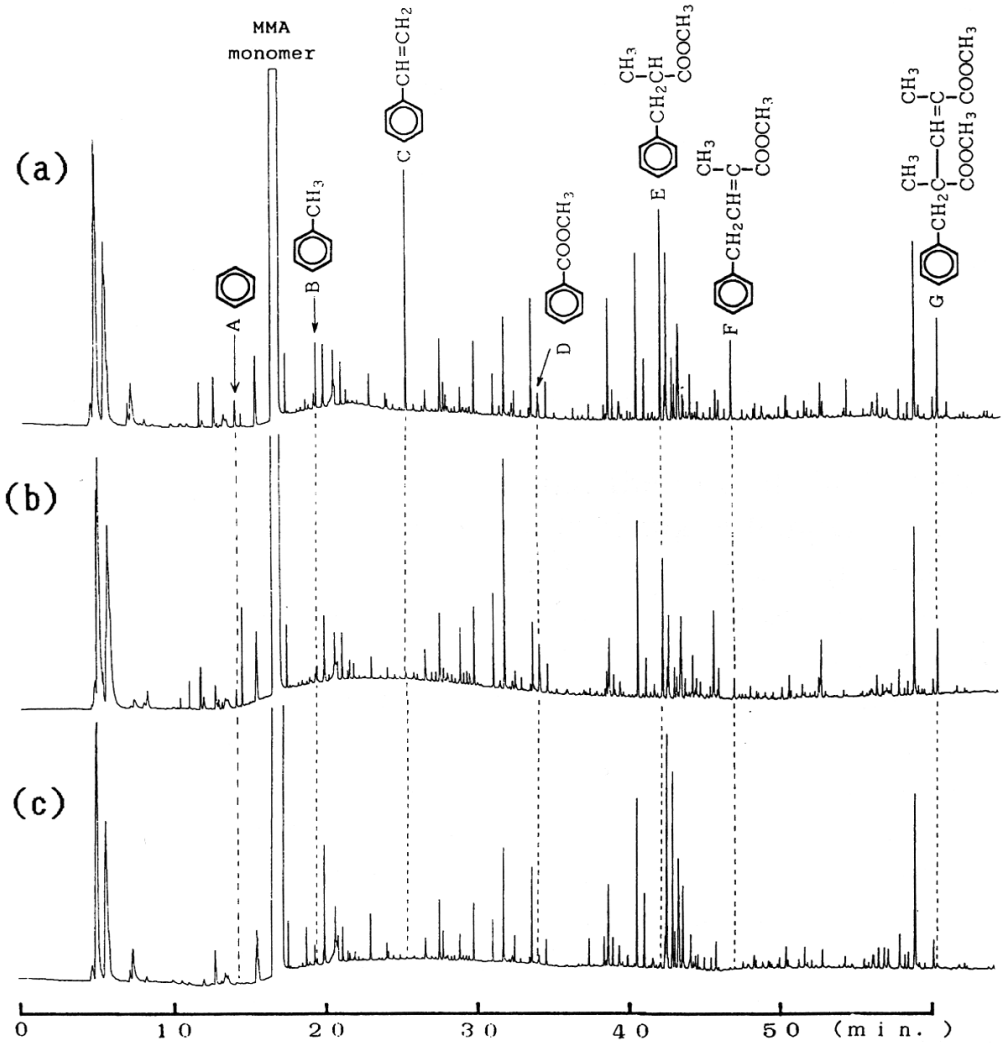

Fig. 1. Pyrograms of PMMA samples obtained at 460ºC

(a) polymerized in toluene,
(b) polymerized in benzene, and
(c) polymerized without any initiator.

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-038E

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A-3

Problem: Is there a simple analytical method to observe the constituent monomers of polybutylene terephthalate (PBT)?

Analysis: When analyzing condensation polymers such as polybutylene terephthalate (PBT) by Py-GC technique, reactive pyrolysis in the presence of tetramethyl ammonium hydroxide (TMAH) gives constituent monomer of methyl ester.

Result: Fig. 1 shows a pyrogram obtained by flash pyrolysis of PBT, and Fig 2 shows a pyrogram obtained by reactive pyrolysis in the presence of TMAH. Flash pyrolysis technique gave products arising from decomposition and decarboxylation of ester group, but no monomer. On the other hand, reactive pyrolysis gave PBT constituent monomer of dimethyl derivatives of terephthalic acid and mono and dimethyl derivatives of 1,4-butanediol.

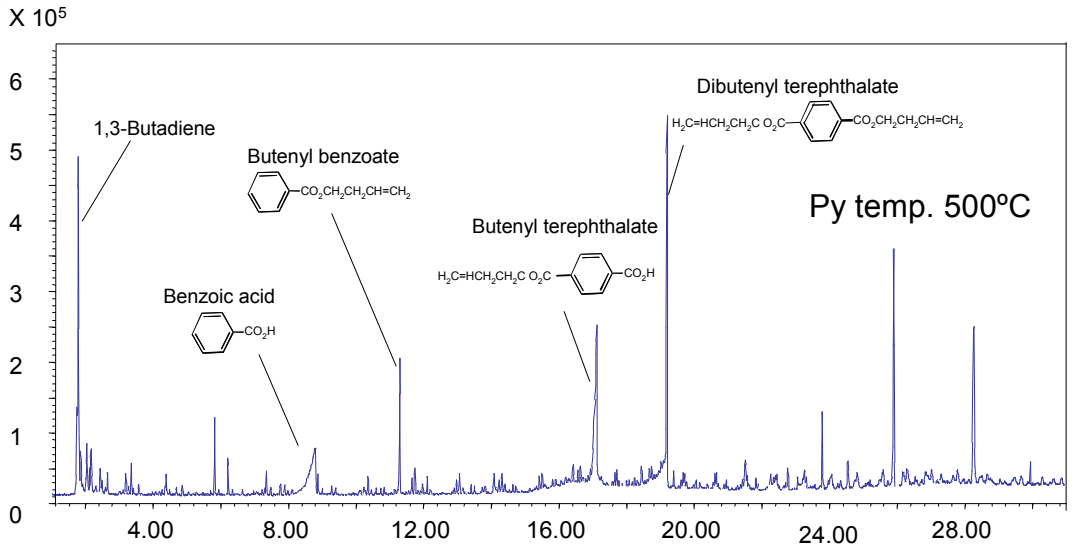

Fig. 1. Pyrogram obtained by flash pyrolysis of PBT

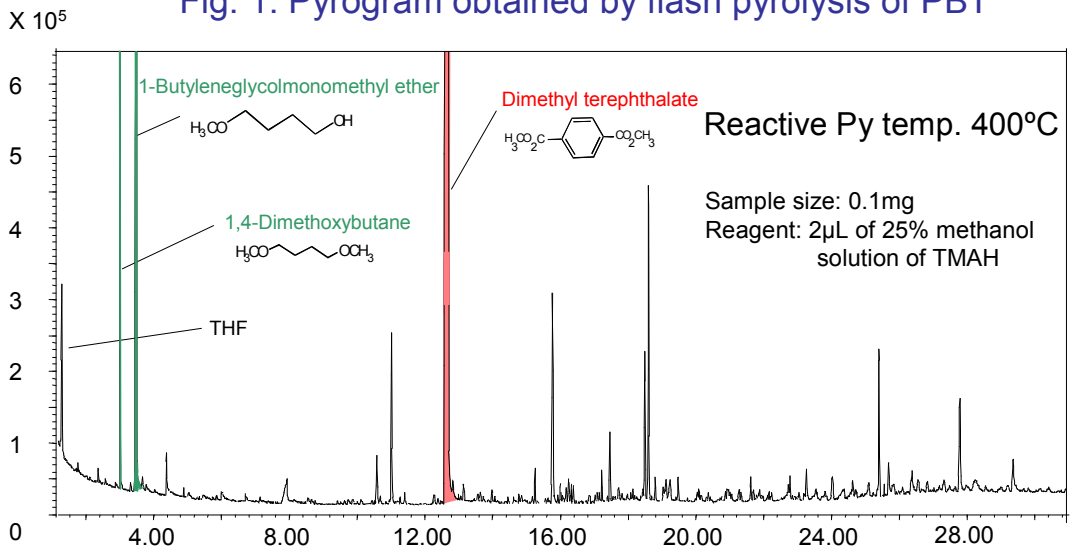

Fig. 2. Pyrogram obtained by reactive pyrolysis of PBT

Carrier gas: He, Injection port pressure: 103kPa, Split ratio: 1/60,
Separation column: Ultra ALLOY$^+$-5 (5% diphenyldimethylpolysiloxane)
L=30m, Id=0.25mm, df=0.25µm, GC oven temp: 38ºC~300ºC (20ºC /min)

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-005E

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A-4

Problem: Is there a technique to obtain information about the sequence distributions of polyacetal (PA)?

Analysis: Multi-component copolymers of PA, containing 1-9 mol% of oxyethylene units [(-OCH2CH2-)(E)] against the main chain oxymethylene units [(-OCH2-)(F)] , are analyzed. The PA sample combined with solid cobalt sulfate (CoSO•7H2O) catalyst is frozen and pulverized. About 100 µg of the powder sample is placed in the sample cup prior to reactive pyrolysis GC/MS at 400ºC.

Result: The pyrogram from the reactive pyrolysis GC/MS for the PA sample is shown in Fig.1. A series of cyclic ethers consisting of E and F units are observed. This reflects the sequence structures of E units in the original polymer chain. From the relative peak intensity of these cyclic ethers, it is possible to estimate the E unit content in the polymer sample as well as the sequence distributions.

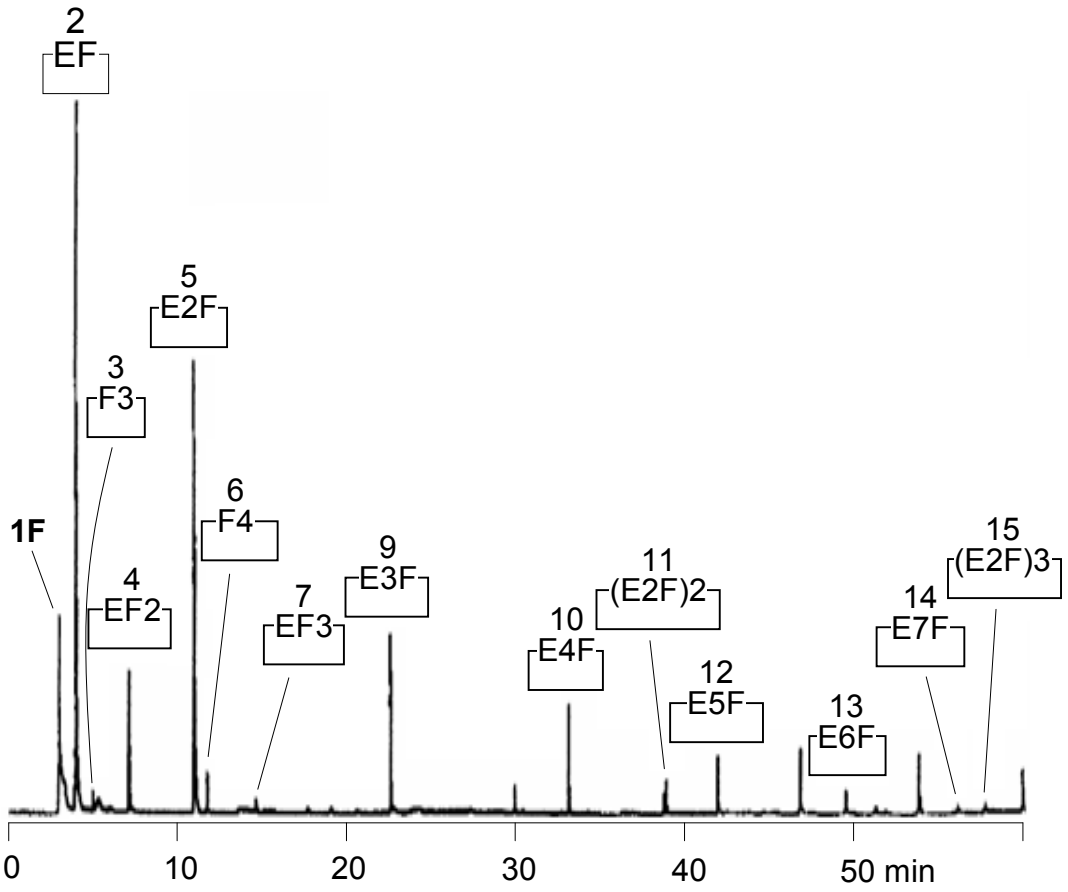


Fig. 1. Pyrogram of copolyacetal by reactive pyrolysis

Pyrolysis temp.; 400ºC, GC oven temp.: 50ºC-(5ºC/min)-300ºC,
Carrier gas flow rate: 50 ml/min, Separation column: poly(methylphenylsiloxane)
L=50 m, id=0.25 mm, di= 0.25 um, Column flow rate: 1.0 ml/min

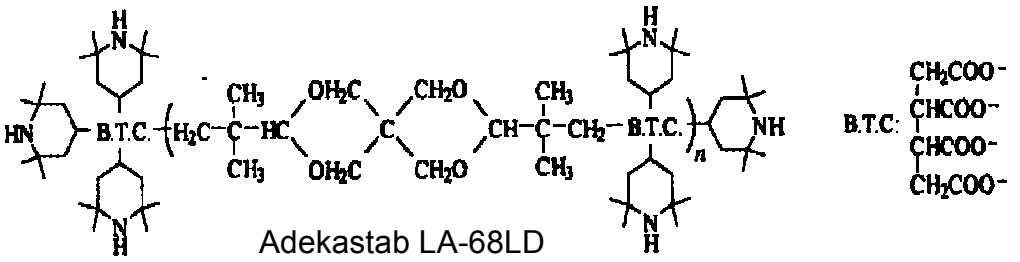
Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-013E

A-5

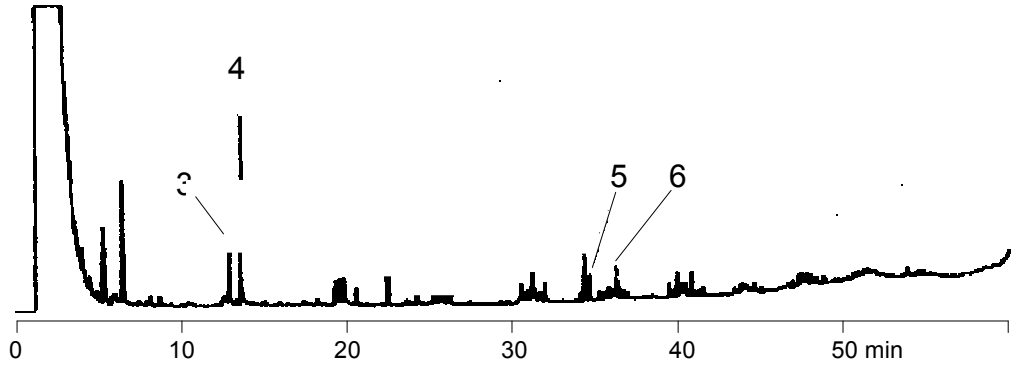
Problem: How is hindered-amine light stabilizer (HALS) in polypropylene (PP) analyzed?

Analysis: Adekastab LA-68LD [MW=1900] as a high molecular weight HALS, and Irganox 1010 and irgafos 168 as antioxidants were added to a PP polymer sample. Then TMAH is added and the PP is analyzed by reactive thermal desorption GC (RTD-GC).

Result: Fig. 1 shows a typical chromatogram of a PP sample containing 10,000 ppm of HALS obtained by RTD-GC in the presence of TMAH at 300ºC. On this chromatogram, the reaction products originated from piperidine (peaks 3 and 4) and spiro ring (peaks 5 and 6) moieties in the original HALS molecule were clearly observed without interferences from pyrolyzates of the substrate PP polymer backbone. The precision was as good as 5% RSD or less.



Adekastab LA-68LD



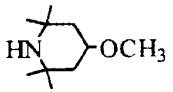
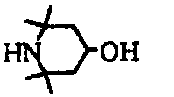
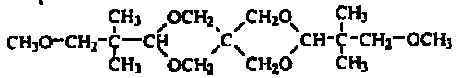
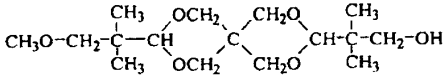
3	
4	
5	
6	
i, j	Peaks derived from Irgafos 168
k	Peaks derived from Irganox 1010

Fig. 1. Typical pyrogram of a polypropyrene sample obtained by RTD-GC

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-017E

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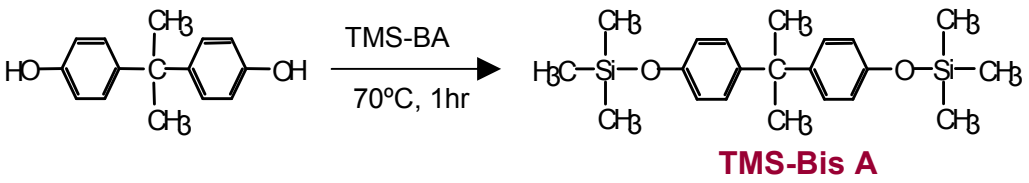
A-6

Problem: What is the best analytical method to determine the residual bisphenol A in polycarbonate (PC)?

Analysis: When thermal desorption (TD)-GC/MS is used, a small amount of Bis A is also generated as a decomposition product of PC making the determination difficult. Here, Residual Bis A is converted to a thermally stable trimethylsilyl derivative. A 10 mg of the PC sample is placed in a vial along with 700 µL of dichloromethane. 300 µL of N,O-bis(trimethylsilyl)acetamide (TMS-BA) is then added. The vial is heated at 70ºC for 1 hour. 10 µL of the reaction mixture was placed in a sample cup for TD-GC/MS analysis.

Result: Scheme 1 shows the reaction products from the TMS-derivatization of Bis A. Fig. 1 shows the chromatogram obtained by TD-GC/MS of the reaction products. As shown in Scheme 1, hydroxyl groups at both ends of Bis A were TMS-derivatized. Using an absolute calibration curve obtained using standard Bis A reagent, the concentration of Bis A in PC was found to be 1,170 ppm, with very good reproducibility (RSD=4.7%, n=5).



Scheme 1. TMS-derivatization of Bisphenol A

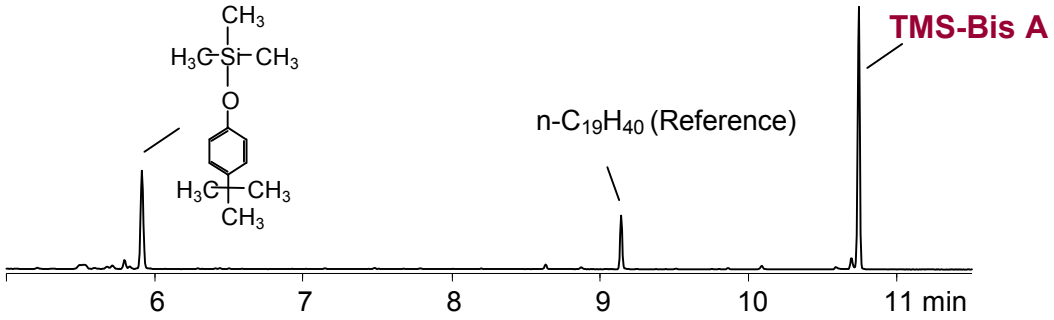


Fig. 1. Chromatogram of TMS-derivatized PC sample obtained by TD-GC/MS

Pyrolyzer furnace temp.: 100-300ºC (100ºC/min), GC oven temp.: 100-300ºC (20ºC/min, 5 min hold)
Separation column: Ultra ALLOY-5 (5% diphenyl 95% dimethylpolysiloxane,
L=30 m, id.=0.25 mm, df=0.25 µm), Carrier gas flow rate: 1.0 mL/min, split ratio: 1/50

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-020E

A-7

Problem: How can the average molecular weight of polycarbonate be determined?

Analysis: A polycarbonate (PC) sample synthesized using the solvent method (SM) was used. About 50 µg of a freezer-milled PC sample was subjected to reactive Py-GC at 400ºC in the presence of 1 µL of 25wt% TMAH methanol solution.

Result: Figure 1 shows a pyrogram of the PC sample obtained at 400ºC in the presence of TMAH. In this pyrogram, *p-tert*-butylanisole (peak A) and the dimethylether of bisphenol-A (peak B), derived from the end groups and the main chain of the PC sample are clearly observed. Because both terminals in the SM-PC molecules are completely end-capped with *p-tert*-butylphenoxy groups, the average molecular weight of the sample (*Mn*) can be estimated from the two peak intensities (Equations 1 and 2): where *DP* is the degree of polymerization, I_A and I_B are the intensities of peaks A and B, respectively, and the divisors 10.2 and 15.4 are effective carbon numbers (ECN) of the respective compounds for a flame ionization detector. The values of 254 and 326 in Eq. 2 are the MWs of the monomer unit and the two end groups, respectively.

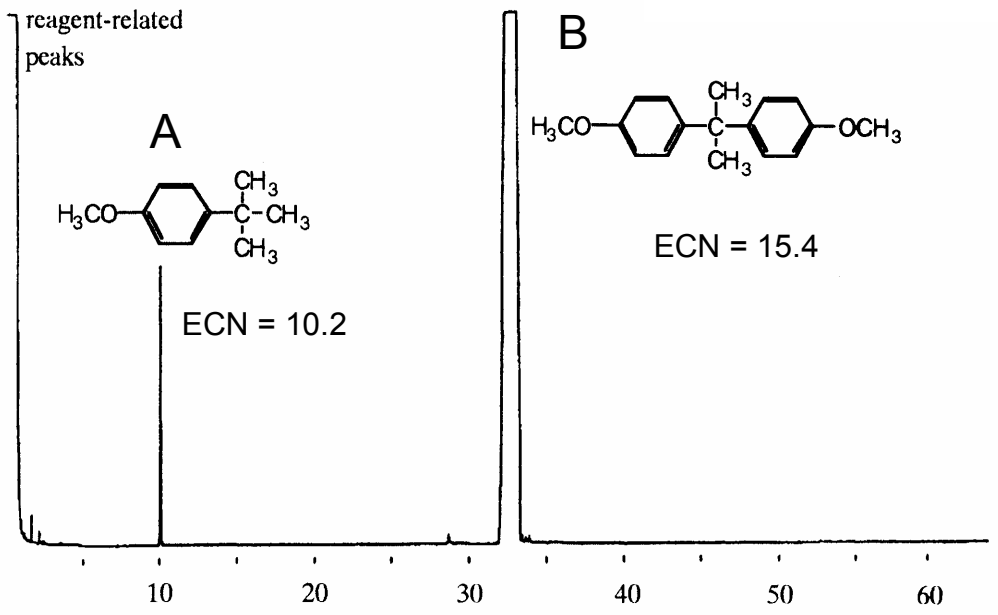


Fig. 1. Pyrograms of PC sample obtained at 400ºC in the presence of TMAH.

Pyrolysis temp. : 400ºC, GC oven temp. : 50ºC- (4 ºC/min)-300ºC
Separation column : Poly(dimethylsiloxane), Length 25mm, 0.25mm i.d., Film thickness 0.25µm
Carrier gas flow : 50 ml/min, Column flow : 1.3 ml/min, Detector: FID

$$DP = \frac{I_B/15.4}{(I_A/10.2)/2} \qquad (1)$$

$$\overline{M_n} = DP \times 254 + 326 \qquad (2)$$

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-015E

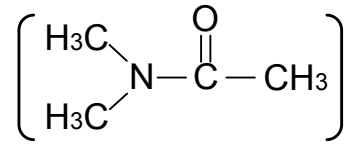
A-8

Problem: Is it possible to analyze compounds out-gassing during the curing of polyimide?

Analysis: Microgram quantities of the sample containing bisphenyl tetracarboxylic acid di-anhydride (BPDA) and sulfonyl bisbenzamine (3,3-DDS) are placed in a sample cup. EGA is performed during the thermal polymerization of the mixture.

Result: Fig.1 shows that polyimide is synthesized when the mixture is heated using a two step process. Fig.2 presents the thermograms for various out-gassing compounds formed during the preparation of polyimide. This result demonstrates that DMAA* and CO2 are formed during the first heating process and SO2 and aniline are generated during the second heating process.

***DMAA: dimethylacetamide**



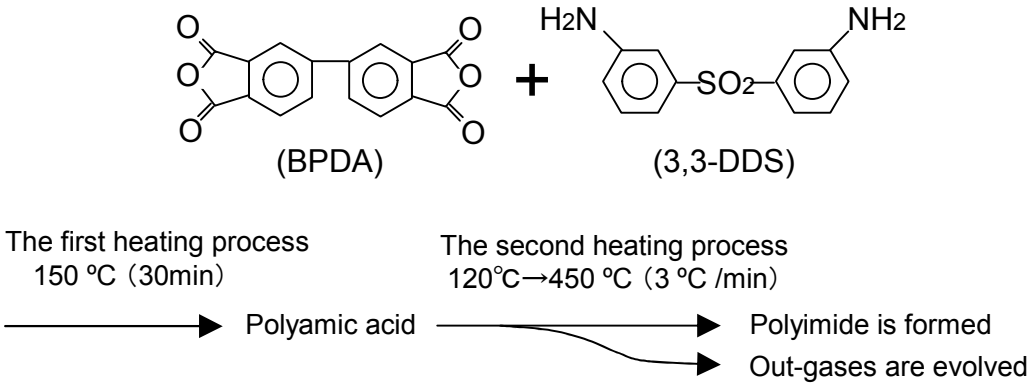


Fig. 1. The synthetic process of polyimide

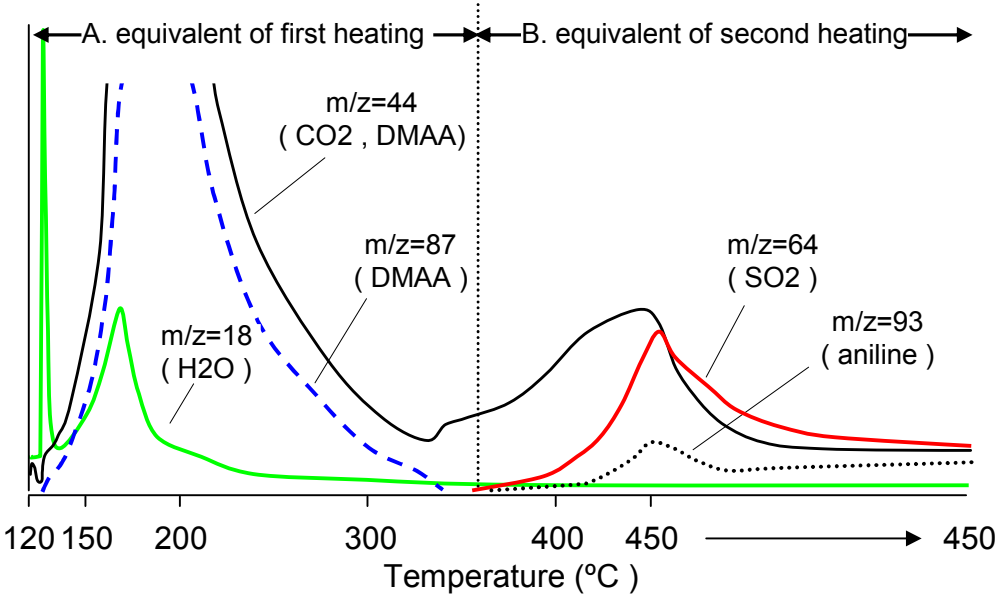


Fig. 2. Thermogram with mass chromatogram in the process of polyimide synthesis

Ref: Multi-functional Pyrolyzer® Technical Note, PYA3-002E

A-9

Problem: Chitin is an important amino polysaccharide and is abundant in nature. How can it be analyzed?

Analysis: Partially deacetylated chitin was commercially obtained. The average degree of N-acetylation (DA) of the chitin was determined by ^{1}H NMR and Py-GC equipped with Multi-Shot pyrolyzer (pyrolyzer temp., 450ºC, He carrier gas). The extent of ester group introduction was estimated by ^{1}H NMR and Py-GC.

Result: The polymer reaction of 1 with ethyl acrylate to the D-glucosamine residue was carried out at 40ºC (Fig. 1). The results are summarized in Table 1. Hydrolysis of pendant ester groups of the product was observed in phosphate buffer solution, while 2 (Fig. 1) was successfully obtained in the solvent containing methanol (run No's. 2 and 3 in Table 1). It was found that the Michael addition proceeded exclusively at the amino groups of 1. Degrees of substitution (DS) to the amino group of the D-glucosamine residue of 2 were determined by ^{1}H NMR. DS values determined based on -$NHCH_2$- were further supported by quantitative analysis of Py-GC technique. The Py-GC is a powerful and convenient methodology to determine chemical structures without considering physical structures and physical properties of polymers (Table 1)

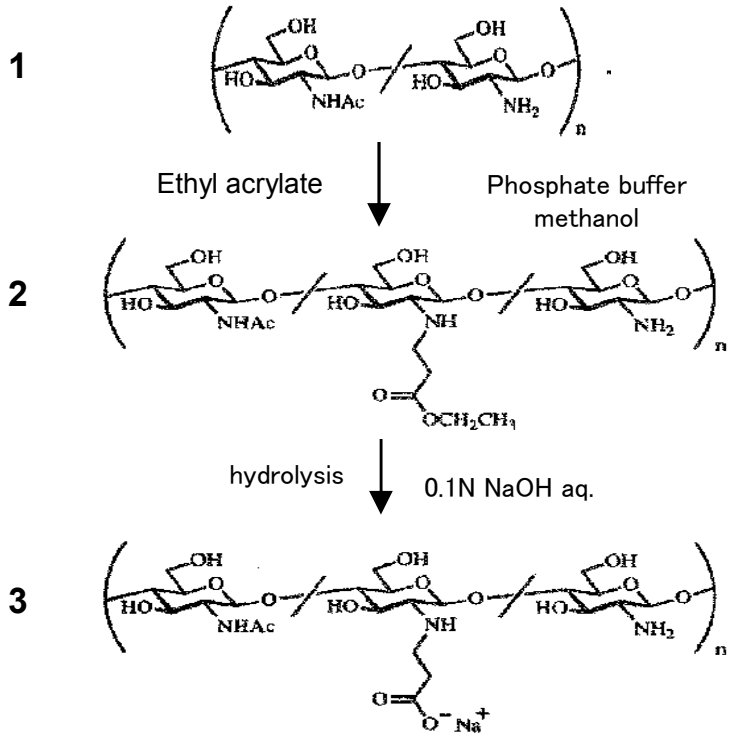


Fig. 1. Synthesis of N-selective ester functionalized chitin derivative and water-soluble carboxyethylchitin

Table 1. Synthesis of N-(2-ethoxycarbonylethyl)chitin (2) of partially deacetylated chitin (1) to ethyl acrylate

Run No.	1		Product polymer			
	mg	-NH2 of **1** mmol	Yield mg (%)	Degrees of substitution		
				^{1}H NMR Based on -$CO_2CH_2CH_2$-	^{1}H NMR Based on -$NHCH_2$-	Py-GC
1	250	0.68	189 (-)	-	0.63	0.69
2	250	0.68	160 (52)	3.2	1.07	0.92
3	250	0.68	178 (59)	1.7	0.87	0.85
4	100	0.24	71 (-)	-	0.68	-

* Reaction condition: Temperature, 40ºC; time. 240hr

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-043E

A-10

Problem: Is there an example of thermal analysis of a blend system based on chitin, polysaccharide?

Analysis: EGA-MS and EGA-MS were applied to the characterization of a chitin-graft-poly(2-methyl-2-oxazoline)/PVA blend system. Chitin-graft-poly(2-methyl-2-oxazoline) was prepared according to the established procedure.

Result: Fig. 1 shows the EGA thermogram of chitin derivative/PVA blends obtained by EGA-MS. The TIC curve of PVA shows two-stage degradation. The thermal degradation of the blends samples also occurs in two stages, reflecting the degradation of both constituent polymers. The thermal degradation products were identified by EGA-MS. Fig. 2 shows the TIC of (a) the eluted products cold-trapped during the first degradation stage from 240 to 340ºC and (b) those eluted during the second stage from 340 to 480ºC for the B(60/40) sample. The major products such as water and various unsaturated and aromatic aldehydes as shown Fig. 2a may be formed during the first degradation stage through dehydration of PVA followed by scission of the resulting polyene chains. On the other hand, various degradation products originating from the chitin derivatives are formed during the second degradation stage as shown in Fig. 2b.

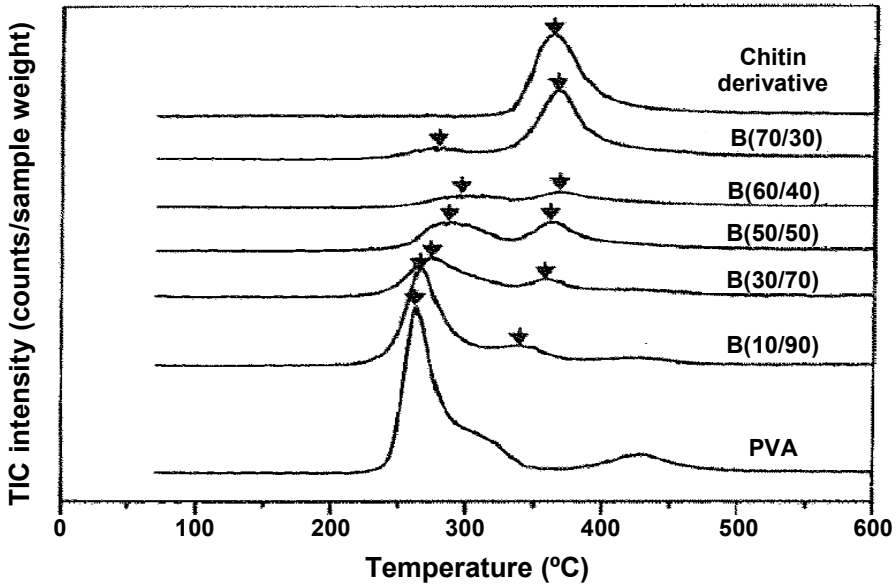


Fig. 1. EGA thermograms of chitin derivative/PVA blend samples obtained by EGA-MS

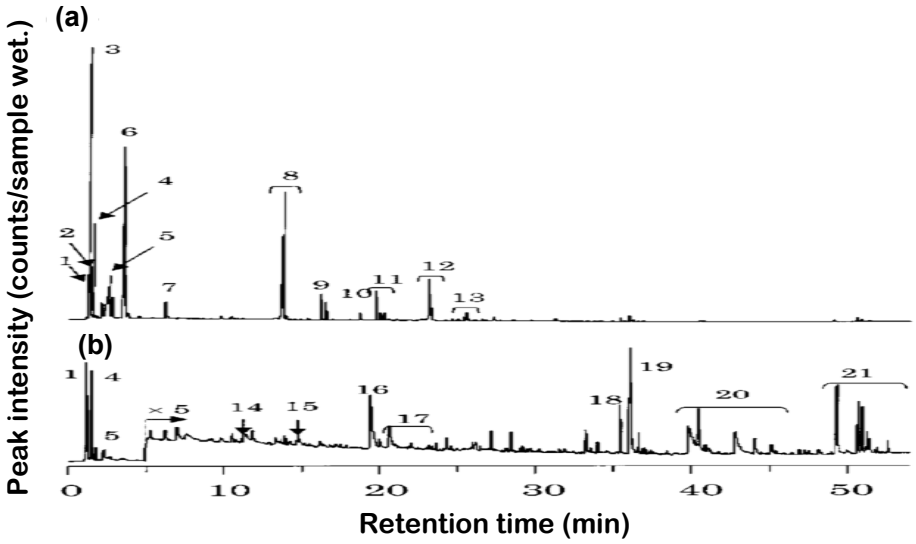


Fig. 2. TICs of degradation products generated from B(60/40) in temperature zones (a) 240- 340ºC and (b) 340-480ºC

Ref: Multi-functional Pyrolyzer® Technical Note, PYA3-008E

B-1

Problem: Is there an example of mutivariate analysis to discriminate natural waxes using the data obtained by reactive-Py-GC in the presence of organic alkali?

Analysis: Two series of carnauba wax samples collected from leaves of Cerifera palm tree in Brazil at two different growing stages were used. Series Y consisted of waxes from younger leaves of the tree while series O consisted of waxes from older leaves. The cryo-milled wax samples were subjected to reactive Py-GC at 500ºC in the presence of 25wt% TMAH (methanol). The resulting pyrograms were processed using the principal component analysis (PCA) software, Ein Sight (InfoMetrix).

Result: A series of the methyl derivatives of acid and alcohol constituents were observed on pyrograms as well-resolved peaks. With peak intensities, chemical compositions were determined. Then, PCA was applied to the data set of chemical composition (33 components) for the six wax samples to visualize the difference among these waxes. Fig. 1 shows the relationship between the 1st and 2nd principal component scores for the wax samples. The two dimensional plot for these waxes clearly indicated the distinction between growth stages.

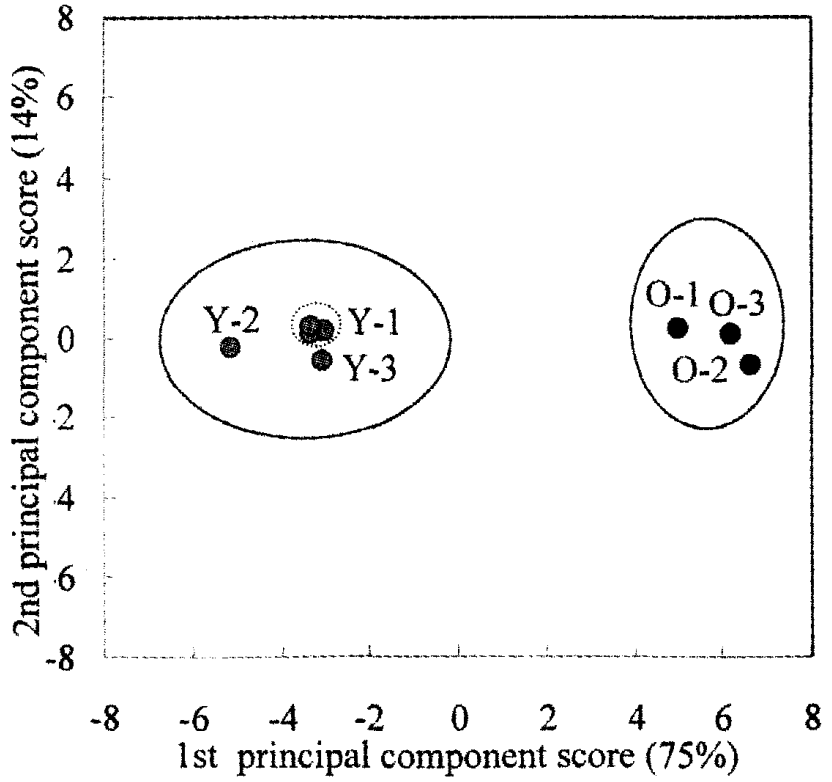


Fig. 1. Discriminative analysis among carnauba wax samples collected from leaves at different growth stage.

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-012E

B-2

Problem: How can an unknown fiber be indentified quickly and accurately using a simple analytical method?

Analysis: The 21 fiber samples used in this study are shown in Fig. 1. Thermograms of these fibers were obtained by EGA. Then a library containing the average mass spectra of the main peaks in each thermogram was created using F-Search. The 21 fibers were differentiated based on the thermal distribution of the evolved gases (i.e. the peak shape of the thermograms) and the F-Search library search results.

Result: One of the 21 fibers was randomly selected to serve as the 'unknown' sample. The 'unknown' samples was then searched using the newly created library. In Fig. 2, three candidates with highest match qualities are shown. Candidates 1 and 2 have match qualities greater than 80, but their mass spectra are too similar to differentiate them. Candidate 1, polyester, had a mass spectrum and thermogram quite similar to that of the unknown sample. When there is more than one candidate with similar thermogram profiles and average mass spectra, they can most likely be differentiated using Py-GC/MS.

• Natural fibers
Animal fibers…Wool, silk
Plant fibers…Cotton, hemp

• Synthetic fibers
Regenerated fibers…Cupra, rayon, polynosic
Semi-synthetic fibers…Acetate, diacetate, vinylon, promix
Synthetic fibers…Nylon 6, polyester (PET), polyester (blended), polypropyrene, polyethylene, acrylic, polyvinyl chloride, polyvinylidene chloride, polychlal

Fig. 1. Fiber samples used in this study

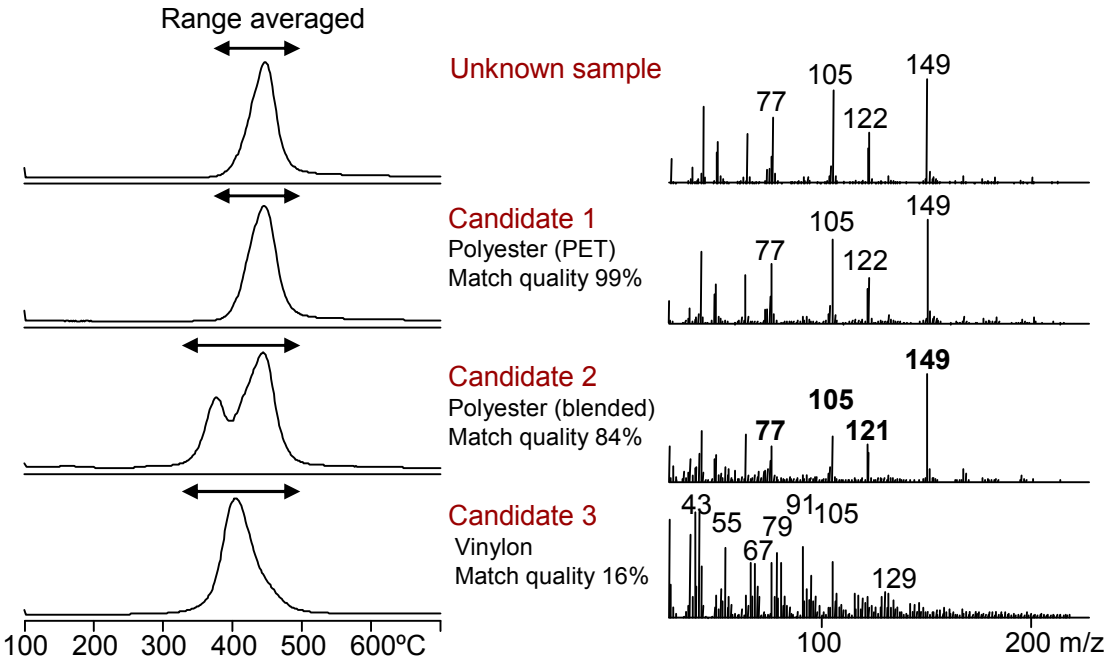


Fig. 2. Comparing EGA thermogram and average mass spectrum of "unknown" fiber with three search candidates with highest match qualities.

Pyrolyzer furnace temp.: 100 - 700ºC (20ºC/min), GC oven temp.: 300ºC, EGA tube: deactivated metal tube L=2.5 m, i.d.=0.15 mm, Column flow rate: 1 mL/min; He, split ratio: 1/50, sample: 300 µg

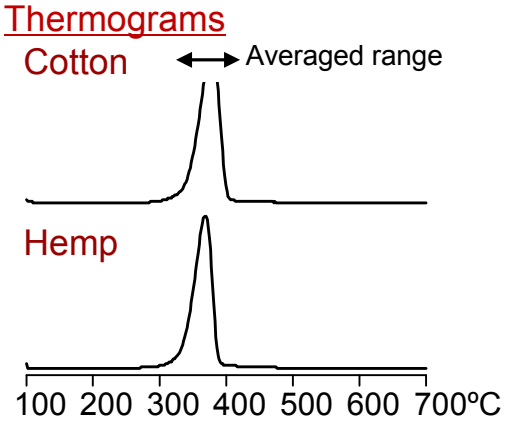
Ref: Multi-functional Pyrolyzer® Technical Note, PYA3-012E

B-3

Problem: Can cotton and hemp be differentiated using a simple analytical technique?

Analysis: Fibers having the same or similar structures are difficult to differentiate using EGA thermograms alone. Therefore, flash pyrolysis (600ºC) of cotton and hemp were obtained.

Result: Fig. 1 compares of the results obtained by EGA-MS for cotton and hemp. Both the thermograms and the averaged mass spectra of the main peaks (300-400ºC) for cotton and hemp are very similar, making it difficult to unequivocally identify the fibers. Pyrograms obtained by Py-GC/MS are shown in Fig. 2. Both pyrograms are similar; levoglucosan is the main peak; however, peaks marked by an "●" are different. Also, there are a series of peaks derived from wax are evident only on the hemp. As shown here, samples with the same major component can be differentiated using Py-GC/MS and focusing on the small differences in the pyrograms.



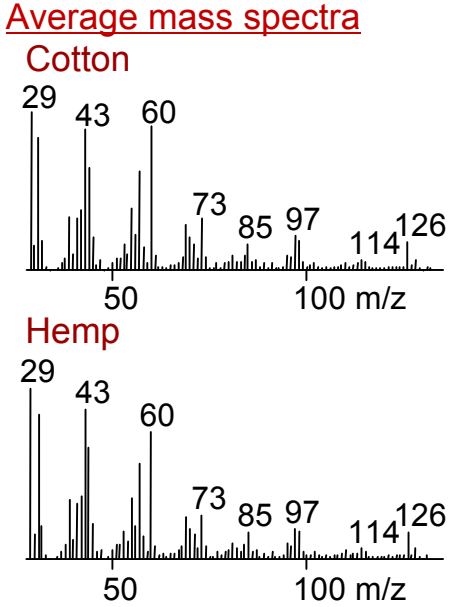


Fig. 1. Comparison of thermograms and averaged mass spectra

Py temp.: 100 - 700ºC (20ºC/min), GC oven temp.: 300ºC
EGA tube: deactivated metal tube, L=2.5 m, i.d.=0.15 mm
Col. flow rate: 1 mL/min; He, split ratio: 1/50, sample: 300 µg

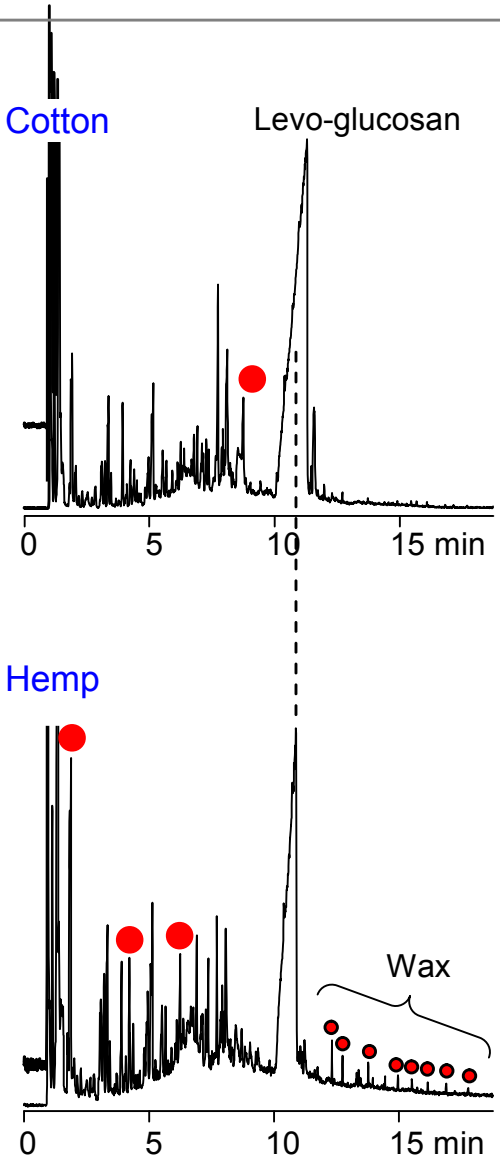


Fig. 2. Comparison of the pyrograms

Py temp.: 600ºC, GC oven: 40 – 320ºC (20ºC/min, 6 min)
Sep. column: UA⁺-5 (5%diphenyl95% dimethyl polysiloxane)
(L=30 m, i.d.=0.25 mm, df=0.25 µm)
Carrier gas flow: 1 mL/min: He, split ratio: 1/50, sample: 100 µg

Ref: Multi-functional Pyrolyzer® Technical Note, PYA3-013E

B-4

Problem: Can black ballpoint pen inks be differentiated by Py-GC/MS? If so, please describe in detail?

Analysis: The pyrograms of 35 inks were used to create an "ink" library. Each ink was scribed onto copy paper. The ink sample was pyrolyzed at 550ºC. The integration-summation (INT-SUM) mass spectrum was calculated for each pyrogram and used to construct an "ink" MS library. One arbitrarily selected ink was used as unknown, and to test the viability of the library.

Result: Pyrograms of the unknown and four inks stored in the library are shown in Figure 1. The major components of each ink are solvents such as phenoxyethanol and diethyl aniline. All elute before 7 min on the pyrogram. Inks A through D showed similar pyrograms; however, small peaks are observed after 7 min. These are dyes and additives and differ from ink to ink. It is difficult to differentiate the inks using only the INT-SUM* mass spectra (Fig. 2(a)), because of the presence of ions m/z 77, 94, and 138 which are from the phenoxyethanol. Thus, a second INT-SUM mass spectra was created from components eluting after 7 min (Fig. 2 (b)). Now, significant differences in match quality are observed and the unknown ink can be easily identified as Ink C.

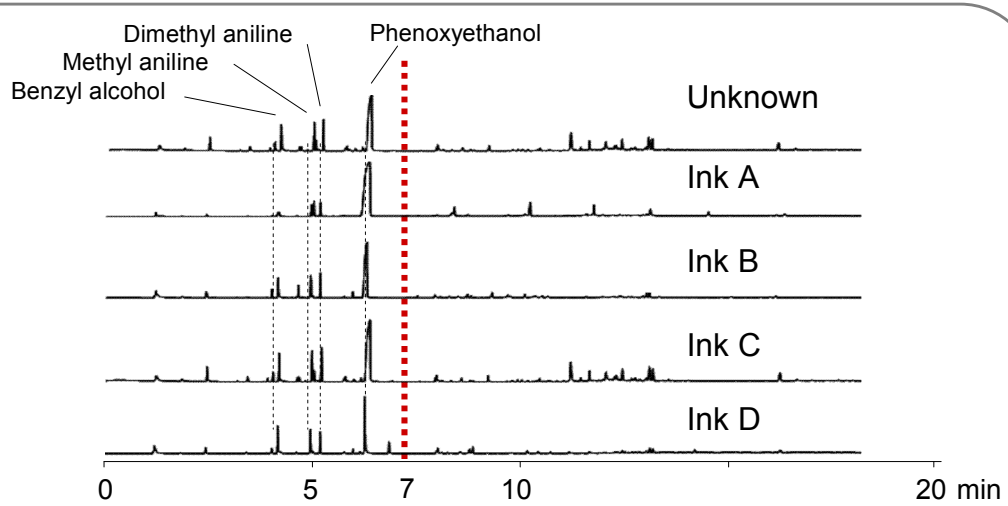
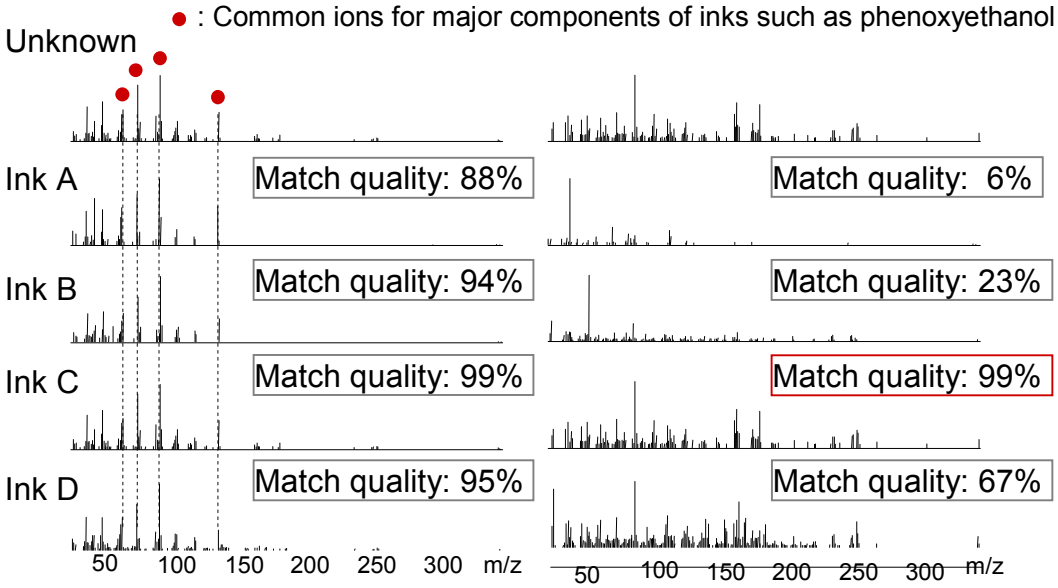


Fig. 1. Pyrograms of oil-based black ballpoint pen inks

Pyrolysis temp.: 550ºC, GC oven: 40 - 300ºC (20ºC/min), Separation column: Ultra ALLOY⁺-5 (5% diphenyl 95% dimethylpolysiloxane), L=30 m, i.d.=0.25 mm, df=0.25 µm, Carrier gas: 1 mL/min, He, Split ratio: 1/50, sample: ca. 200 µg



(a) Mass spectra created from entire pyrogram (0-20 min)

(b) Mass spectra created from pyrograms of components eluting after 7 min.

Fig. 2. Comparison of mass spectra created (a) from entire pyrogram and (b) from components eluting after 7 min.

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-067E

FRONTIER LAB

C-1

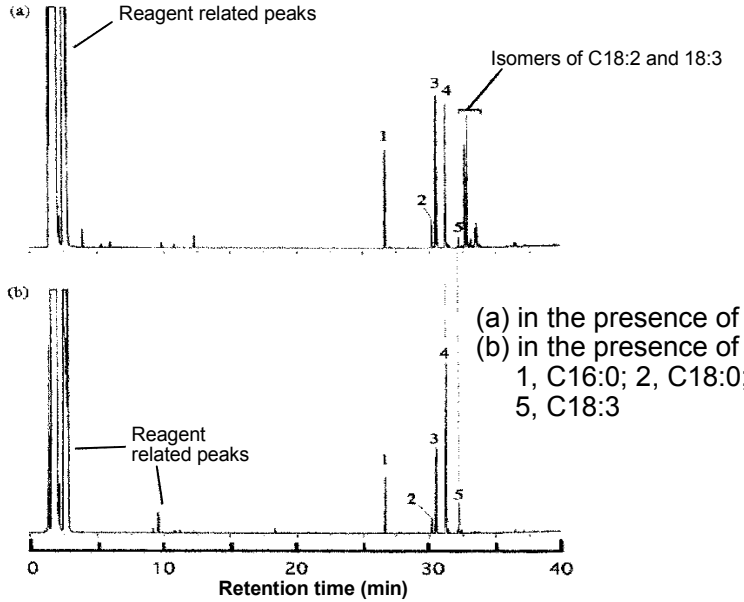
Problem: Is there a simple way to perform compositional analysis of polyunsaturated fatty acid (PUFA) in oils such as soybean oil?

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: Figure 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.

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-009E

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



(a) in the presence of 0.15M of TMAH
(b) in the presence of 0.2M TMSH.
1, C16:0; 2, C18:0; 3, C18:1; 4, C18:2; 5, C18:3

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 18:2&18:3	Total
		Compositions (mol%)						
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.

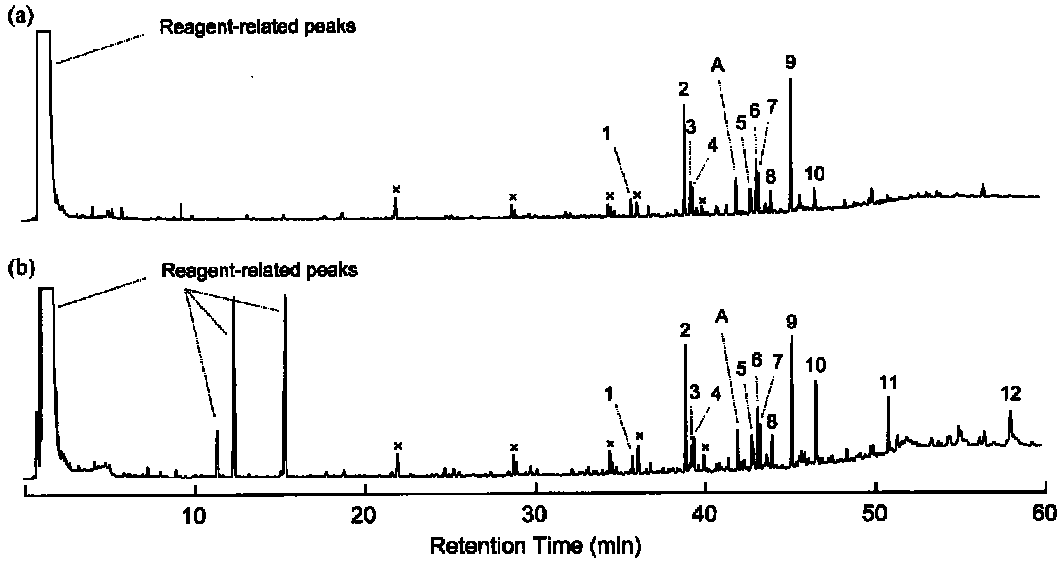
FRONTIER LAB

C-2

Problem: How are lipids in plankton be analyzed using the Multi-Shot pyrolyzer?

Analysis: *Daphnia galeata* individuals cultured in the laboratory were used as plankton samples. As derivatizing reagents, a methanol solution of TMSH and a methanol solution of TMAH were used. Dried zooplankton sample was subjected to reactive Py-GC at 400ºC in the presence of the organic alkali solution.

Result: Figure 1 shows typical pyrograms of two D. galeata individualsh obtained by reactive Py-GC in the presence of (a) TMAH and (b) TMSH at 400 ºC, respectively. On both of the pyrograms, methyl esters of saturated and unsaturated C14 - 18 fatty acids (peaks 1 – 10) were commonly observed. The peaks of EPA (peak 11) and DHA (peak 12) containing 5 and 6 double bonds were clearly observed on the pyrogram (b) obtained with TMSH, while they were virtually missing in the pyrogram (a) using TMAH due to their thermal isomerization and/or degradation. This result demonstrates that THM-GC in the presence of TMSH allowed the highly sensitive detection of a series of fatty acid residues.



Peak 11: eicosapentaenoic acid (EPA; C20:5)
Peak 12: docosahexaenoic acid (DHA; C22:6)

Fig. 1. Chromatogram of zooplankton samples obtained by reactive Py-GC at 400ºC in the presence of (a) TMAH and (b) TMSH.

Pyrolysis temp. : 400ºC, GC oven temp. : 50ºC-(5 ºC/min)-240ºC
Separation column : Ultra ALLOY-CW [poly(ethylene glycol)]
Length 30 m, 0.25 mm i.d., Film thickness 0.25 µm
Carrier gas flow : 50 ml/min, Column flow : 1.0 ml/min

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-018E

C-3

Problem: What is the best method to characterize fatty acids in algae?

Analysis: 0.2 mg of dried algae was placed in a sample cup, 10 µL of trimethylsulfonium hydroxide (TMSH) in methanol (0.2M) was added and the cup was dropped into theMulti-Shot pyrolyzer's furnace (350ºC) in an He atmosphere. The gas-phase reactions occurred instantaneously. The methylated acids were separated and analyzed using GC/MS

Result: The individual fatty acids can easily be identified and quantitated using extracted ion chromatograms. The separation and identification of the isomers is a function of the column's stationary phase, the phase ratio and the GC oven's temperature profile. The distribution of the fatty acids is one of the primary means used to differentiate algae strains.

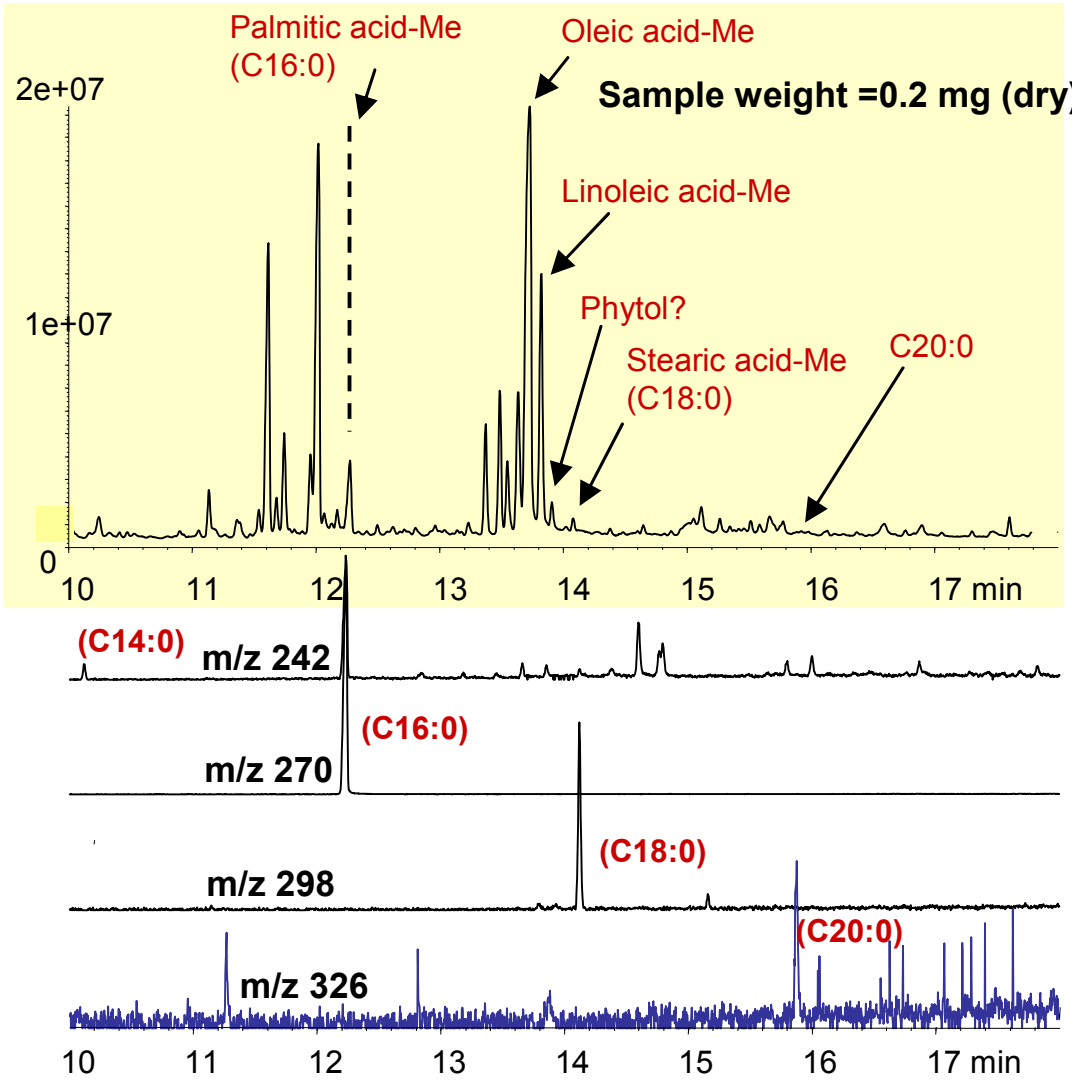


Fig. 1. Pyrogram of dried algae obtained by reactive Py-GC/MS

<Reactive pyrolysis conditions>
Pyrolyzer oven temp.: 350°C, separation column: UA-5 (MS/HT) L=30m, id=0.25mm, df=0.25µm, GC oven temperature: 100~320°C at 10°C/min (10 min hold), He: 1.0 mL/min, split ratio: 1/40, sample weight: ca. 0.2mg (dry), 0.2M TMSH in methanol: 10 µL

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-022E

D-1

Problem: Is there an example in which a ceramic composite material was analyzed by the Multi-Shot Pyrolyzer? If so, please describe.

Analysis: A ceramic composite material was analyzed by EGA-MS technique using analytical conditions summarized in Fig. 1. Peaks on the thermogram were identified by library search using EGA-MS library.

Result: Fig. 1. shows the EGA curve and average spectra of peaks A, B, C, and D observed for the composite material. Background (BG) noise has been subtracted from the average spectra. Figs. 1a and 1b show the results of library search on the spectra using Frontier Lab F-Search system with EGA-MS library. Peaks C and D were found to be PBMA and PS, respectively. Peak A and B are considered to be of low boiling compounds because of their lower elution temperatures. Upon searching the normal MS library (Wiely 275), peak A was judged to be a phthalate, and peak B, saturated hydrocarbons. Library search with a combination of the MS library and EGA-MS library as shown here is extremely useful as the primary search method to determine the composition of an unknown polymer.

Fig. 1a Library search result for peak C

Name	Qual
1. Poly(n-butyl methacrylate) (PBMA)	**72**
2. Poly(2-hydroxyethyl methacrylate) :	4
3. Higher methacrylate copolymer	2

Fig. 1b Library search result for peak D

Name	Qual
1. Polystyrene (PS)	**90**
2. Styrene-ethylene-butadiene-styrene-block copolymer	78
3. Modified poly(phenylene oxide)	64

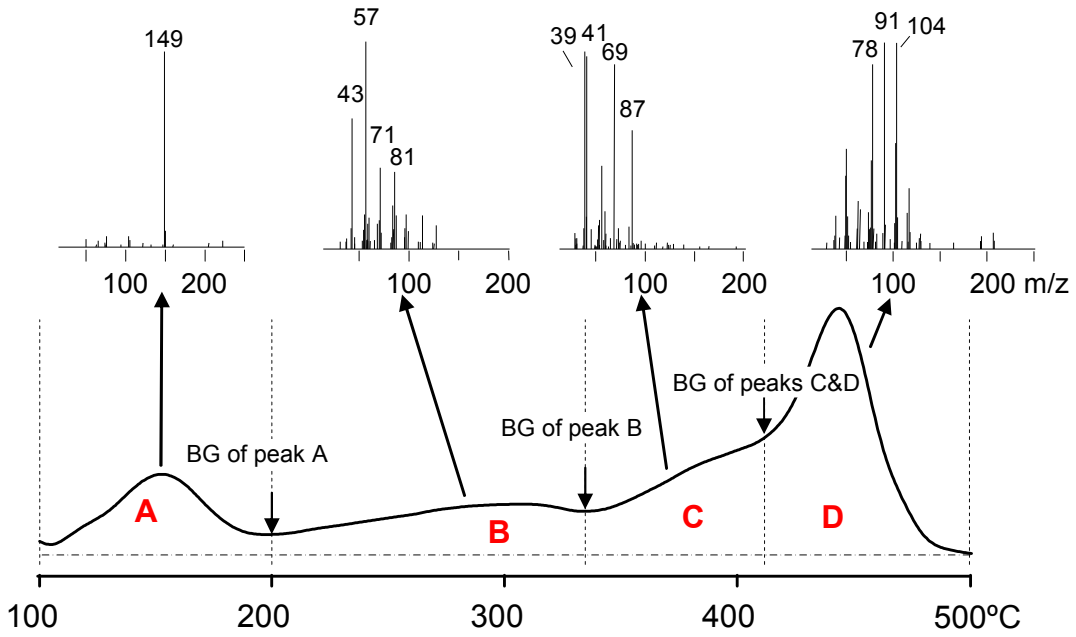


Fig. 1. EGA curve of ceramic composite material (Injection molding)

Pyrolyer furnace temp: 100°C~500°C (20C/min), Carrier gas : He 50kPa, Split ratio: ca. 1/50
EGA tube: id.=0.15 mm, L=2.5m (UADTM-2.5N), GC oven: 300°C, Injection port temp : 320°C,
Sample: ca. 0.5 mg, Detector: MS (m/z=29-400, 0.1 scan/sec), PY-GC interface: 320°C (Auto)

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-010E

D-2

Problem: How can an antioxidant in a polymer be analyzed while avoiding interferences by the polymer backbone?

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-MS) was performed in temperature range 100~600ºC to determine the thermal property of the sample.

Result: The thermogram of the PE sample, obtained by EGA-MS, 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 100-200ºC. This defines the thermal desorption conditions (100-200ºC at 20ºC/min, 3 min hold) for determining BHT in PE.

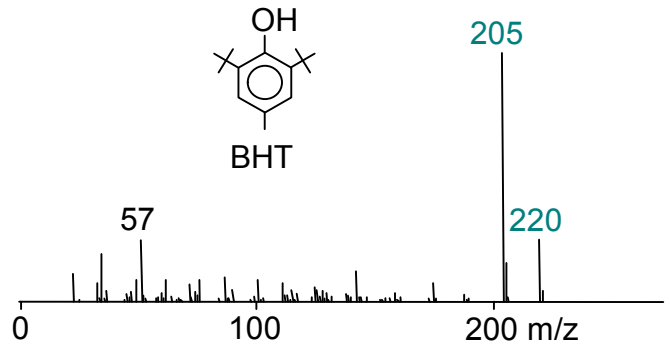


Fig. 1. Chemical structure of BHT and its mass spectrum

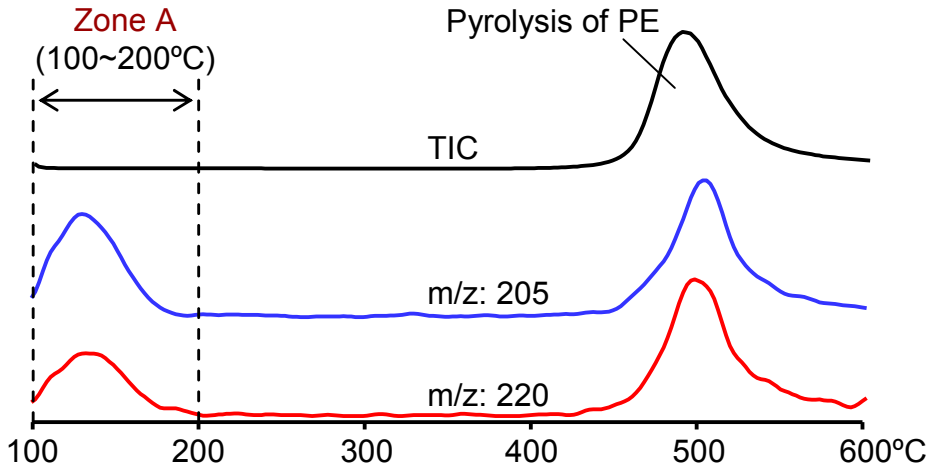


Fig. 2. Thermograms of a PE sample

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

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-055E

D-3

Problem: How are the additives in polystyrene (PS) identified using the Multi-shot pyrolyzer system?

Analysis: A Multi-shot pyrolyzer (model 3030D) is installed on a GC/MS. Both the deactivated metal capillary tube (EGA) and the metal capillary separation column (TD) are interfaced to the MS using a vent-free GC/MS adaptor. 50 µL of a 20 mg/mL dichloromethane solution is added to a sample cup and the solvent is allowed to evaporate prior to analysis. The analytical conditions are provided in the figure captions. F-Search additive library can be used to identify unknown additives in PS. The library includes both chromatographic and mass spectral data for 358 additives.

Result: (EGA)-MS was utilized to determine the thermal desorption zone of the volatile additives - see Fig. 1. This thermal zone ((100-300ºC) was analyzed using TD-GC/MS. Each peak was tentatively identified using the F-Search additive library. Ten "additive" were identified based on mass spectral match quality and retention indices.

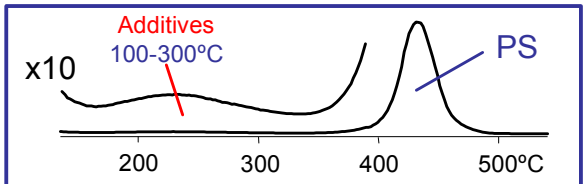


Fig. 1. EGA Thermogram of PS

Py furnace temp.: 100 - 700ºC (20ºC/min),
GC oven temp.: 300ºC,
EGA tube: UADTM-2.5N(L=2.5 m, i.d. 0.15 mm),
column flow rate: 1 mL/min He, split ratio: 1/50,
sample: 0.1 mg

TD-GC/MS: total ion chromatogram

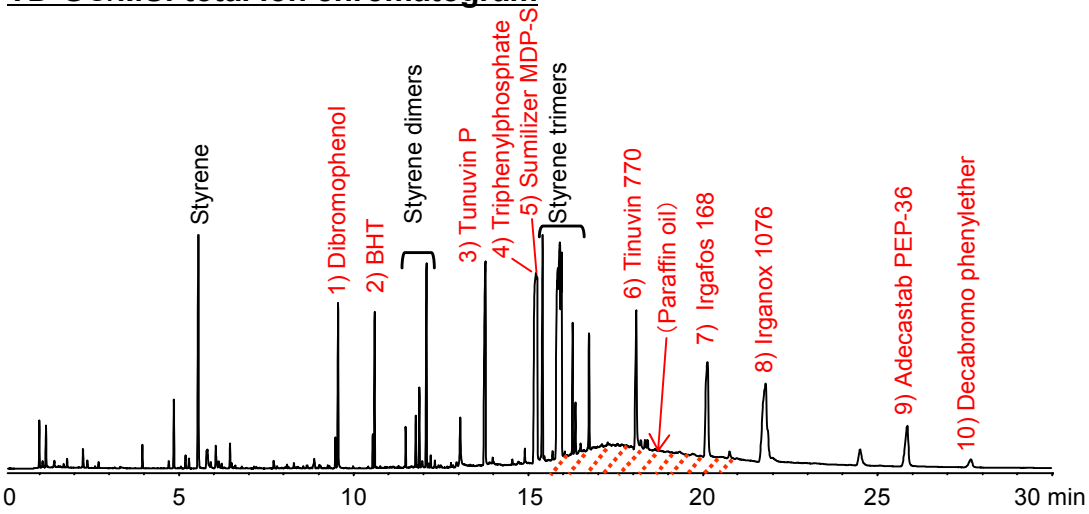


Fig. 2. Library search results

Pyrolyzer temp.: 100 - 300ºC (20ºC/min, 5 min), GC oven temp.: 40ºC (2 min) - 320ºC (20ºC/min), separation column: Ultra ALLOY^{+}-5 (5% diphenyl 95% dimethylpolysiloxane) (L=30 m, i.d.=0.25 mm, df=0.05 µm), column flow rate: 1 mL/min He, split ratio: 1/20, scan rate: 2 scans/sec, scan range: 29 - 810 (m/z), sample: 1 mg

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-066E

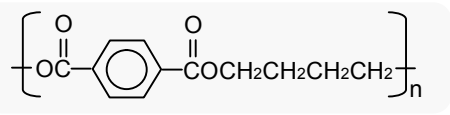
D-4

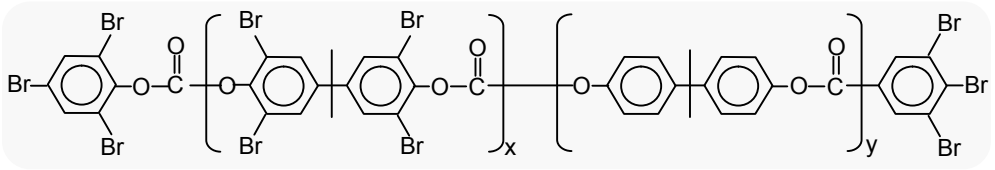
Problem: Have flame retardants in polybutylene terephthalate (PBT) been analyzed by the Multi-Shot pyrolyzer in EGA mode?

Analysis: An example described here is elucidation of flame retardant mechanism of brominated polycarbonate (15%) and antimonious oxide (5%) (Fig. 1) added, as flame retardants, to PBT using Multi-Shot Pyrolyzer.

Result: Fig. 2 shows evolved gas curves of Sb, Br, and C contained in the flame retardant PBT. By the catalytic action of Sb_2O_3, brominated compounds are eluted at lower temperatures than flammable gases such as butadiene and butylene terephthalate produced during the thermal decomposition of PBT, thus it is considered that the flame retardants inhibits the ignition of PBT at the early stage of decomposition. As shown here, observing the elution of targeted elements in the evolved gases by atomic emission detector (AED) provides an insight into the effect of flame retardants.

• Base polymer :
Polybutylene terephthalate (PBT), 80wt%





• Flame retardants :
1) Brominated polycarbonate, 15wt%
2) Antimonious oxide (Sb_2O_3), 5wt%

Copolymer of tetra-bromo-bis-phenol A and bis-phenol A (2/1);
Average degree of polymerization = 3

Fig. 1. Base polymer and structure of flame retardant

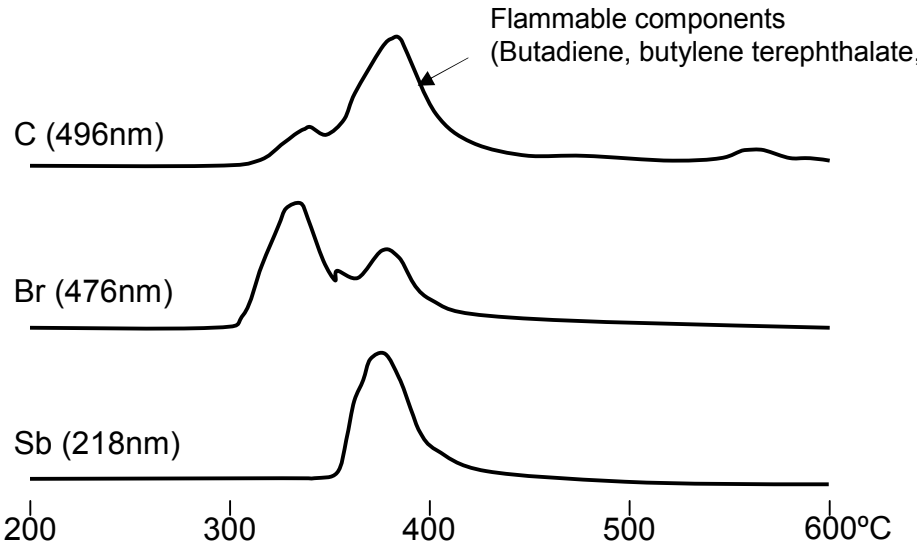


Fig. 2. Thermal decomposition of flame retardant PBT observed by evolved gas analysis (EGA)
(Detector : AED(Atomic Emission Detector), Atmosphere gas : He)

Ref: Multi-functional Pyrolyzer® Technical Note, PYA3-003E

FRONTIER LAB

D-5

Problem: What is the best way to obtain the thermal properties of a flame retardant polybutylene terephthalate (PBT)?

Analysis: The chromatograms were obtained by programmed heating of the pyrolyzer furnace from 60 to 700ºC, followed by GC analysis of resultant evolved gases that were trapped at the head of GC column.

Result: Fig. 1 shows chromatograms of evolved gases from flame retardant PBT. In addition to decomposed products from PBT, brominated phenols, thermal decomposition products of brominated PC, and SbBr3, produced from brominated PC and antimonious oxide, were also detected. Fig. 2 shows evolved gas curves obtained using MS as a detector (TIC) and mass chromatograms of characteristic ions of species A~E (shown in Fig 1). Dibromo phenol was detected at 350ºC; while flammable gases, hydrogen bromide, and antimony bromide, were detected at 380ºC. Thus, in evolved gas analysis using MS, obtaining characteristic ions of target species provides an insight into thermal properties of polymeric materials.

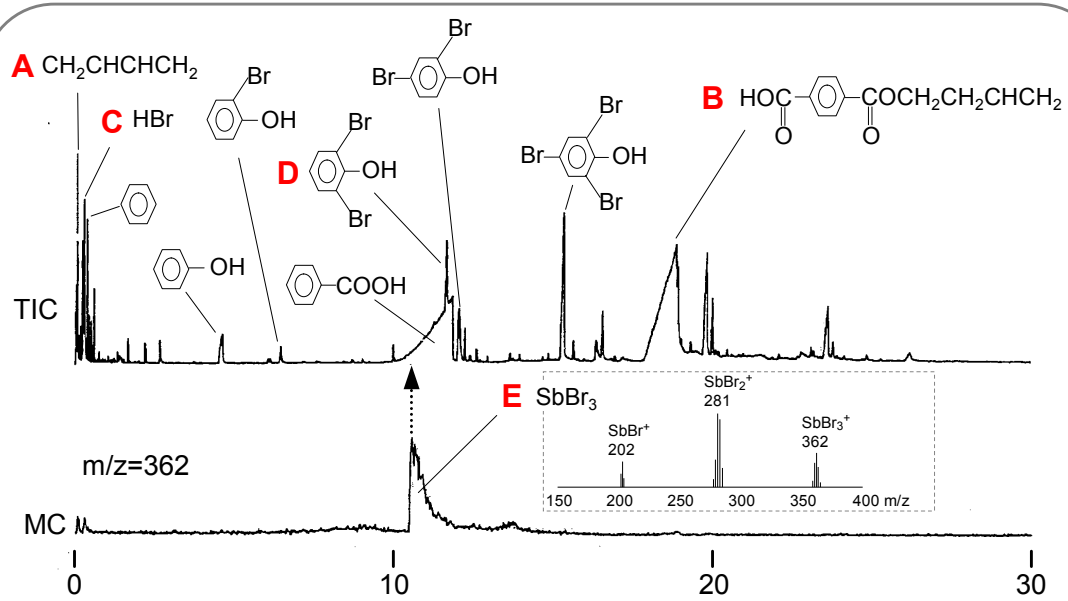


Fig. 1. Chromatograms of thermal decomposition products of flame retardant PBT

Components evolved in 60~700ºC range in He were trapped in Liq. N_2, then analyzed by GC/MS

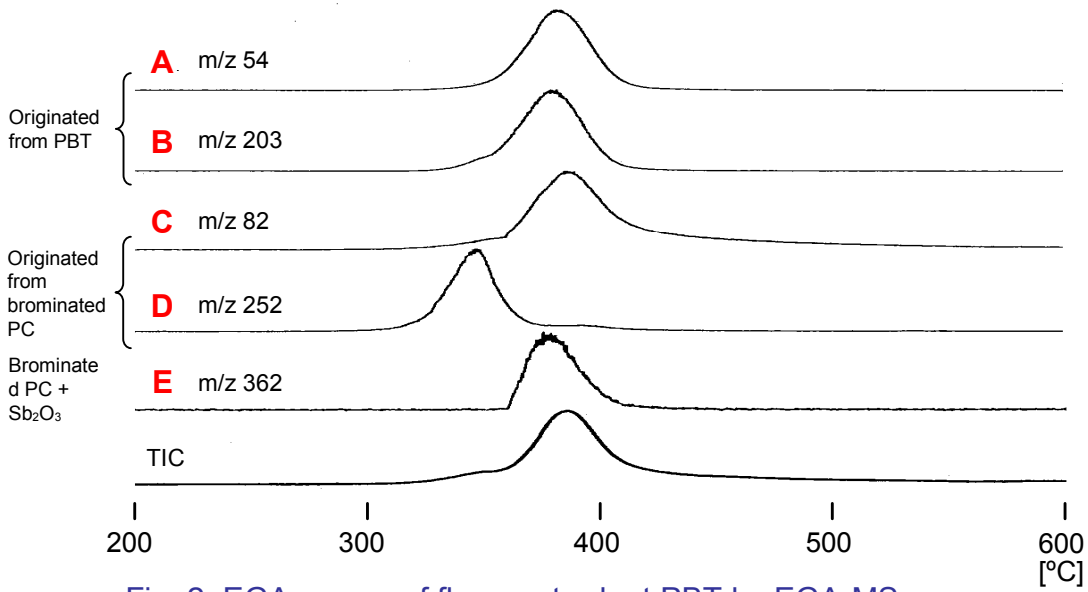


Fig. 2. EGA curves of flame retardant PBT by EGA-MS

Ref: Multi-functional Pyrolyzer® Technical Note, PYA3-004E

FRONTIER LAB

E-1

Problem: Shellac is a thermosetting resin of animal origin found in south-east Asia. Is there a simple analytical method for that?

Analysis: The reactive Py-GC in the presence of tetramethylammonium hydroxide (TMAH) was applied to the compositional analysis of shellac. Eight shellac samples from India and Thailand were used. Samples were cryo-milled into a fine powder (<60 mesh). About 90µg of sample and 2µL of TMAH solution were introduced into the pyrolyzer for pyrolysis at 400ºC.

Result: Figure 1 shows typical pyrograms of Indian shellac at 400ºC with and without addition of TMAH. In Figure 1a, only weak and broad peaks of terpenic acids and wax components were observed, while in Fig 1b, a series of sharp peaks due to the methyl derivatives of shellac constituents were observed with better resolution and higher sensitivity. With these results shown, this technique was found to provide simple and quick compositional analysis of shellac.

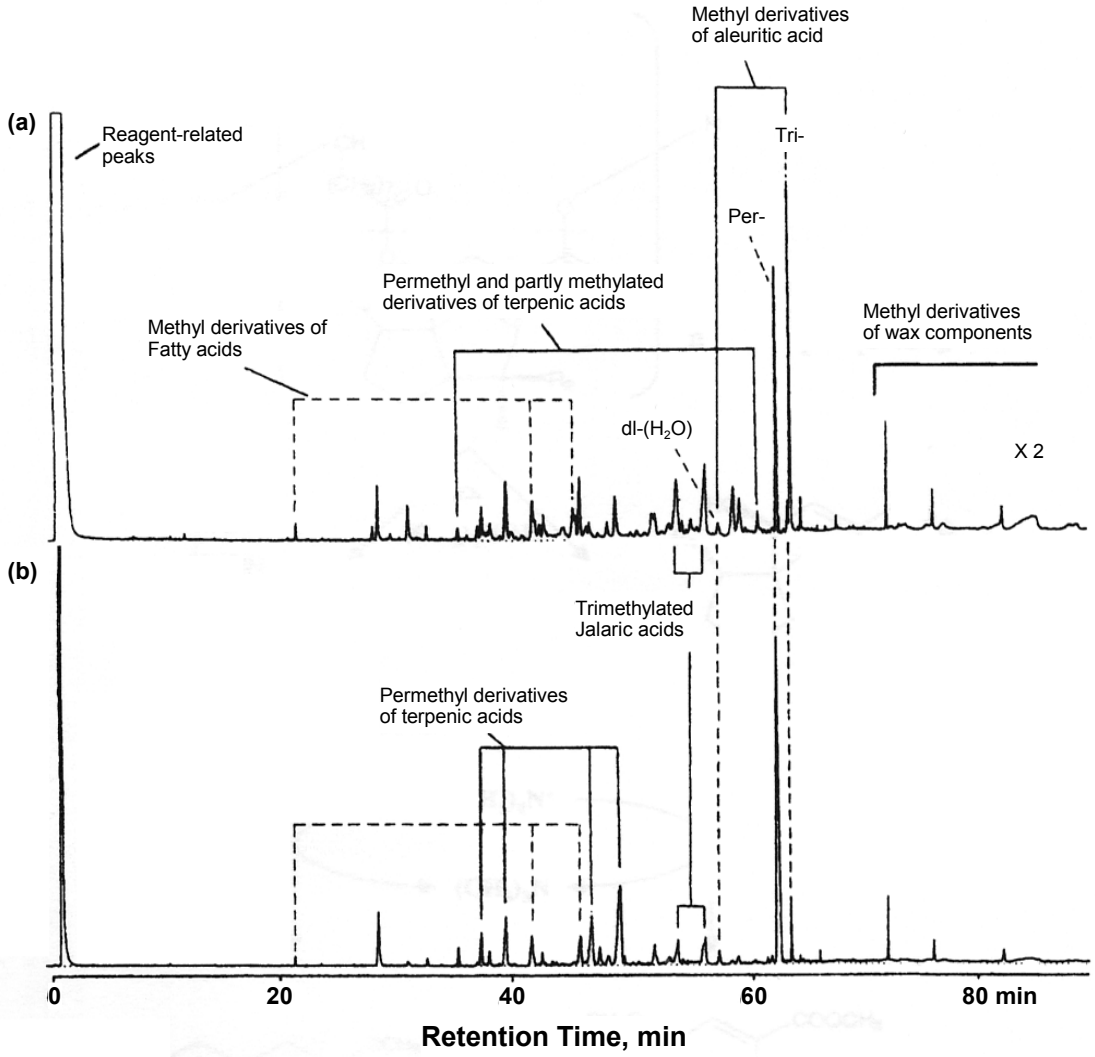


Fig. 1. Typical pyrograms of Indian Shellac obtained at 400°C

(a) In the absence of TMAH, (b) In the presence of TMAH solution

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-008E

E-2

Problem: Is there a way to characterize the network structure of UV cured acrylic ester resin?

Analysis: About 100 µg of the powder of a UV-cured resin prepared from polyethylene-glycol diacrylate and morpholino-type photoinitiator (IRGACURE 907) is subjected to reactive Py-GC at 400ºC in the presence of 4 µL of TMAH in methanol (25%).

Result: Fig. 1 shows a typical pyrogram of the UV-cured resin. In this pyrogram, minor but distinct peaks of various methyl acrylate (MA) oligomers directly reflecting the cross-linked structures are observed along with a series of methoxy derivatives of ethyleneglycol oligomers. The derivatives originate from the main chain after chemolysis at the acrylate linkages (Scheme 1). The relative peak intensities of the various MA units enable the analyst to determine the chain length distribution of the network junctions contained in the UV-cured resin..

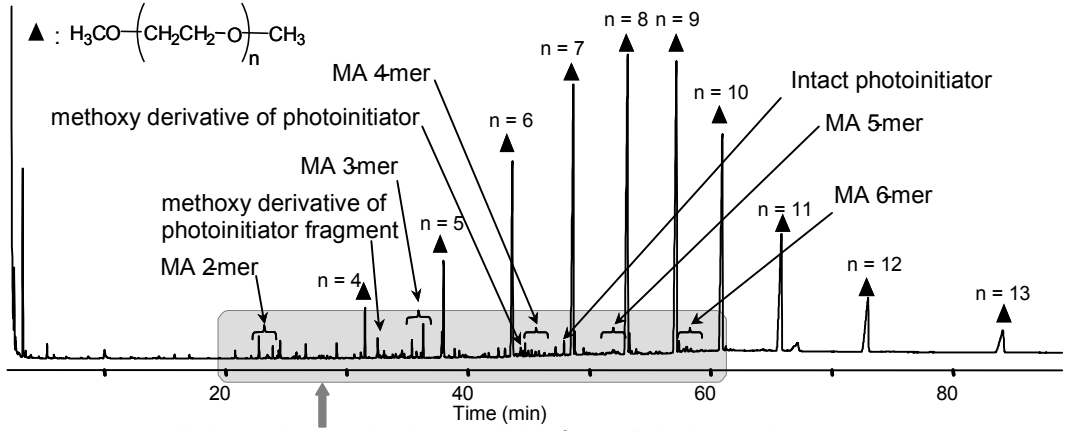
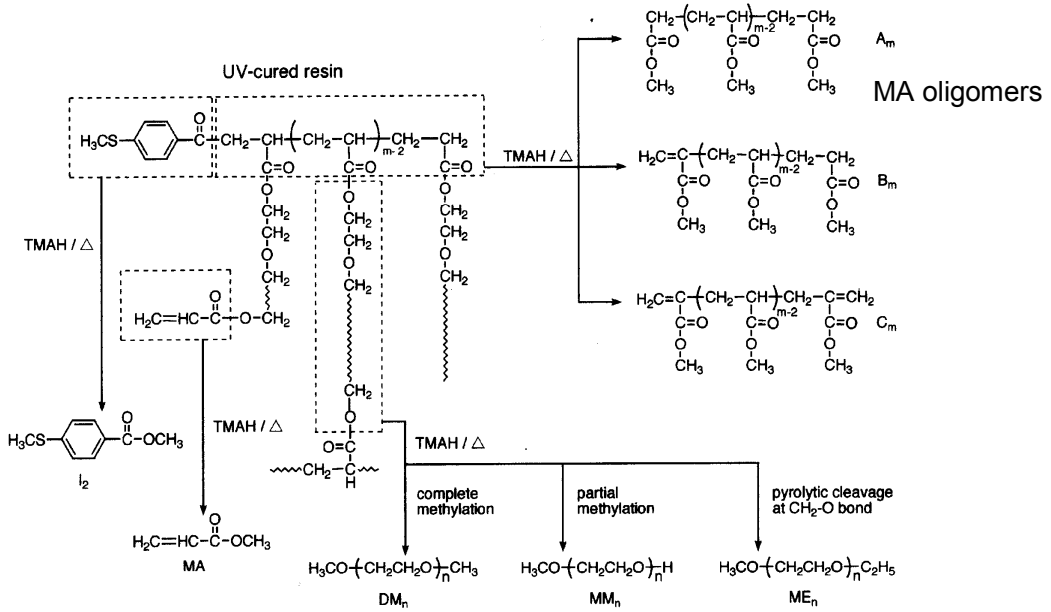


Fig. 1. Typical pyrogram of UV-cured resin prepared from polyethyleneglycol diacrylate and morpholino-type photo-initiator.

Pyrolysis temp.: 400ºC, GC oven temp.: 35ºC (6 min)-(5 ºC/min)-340ºC
Separation column: Poly(5% diphenyldimethylsiloxane), L=30 m, id=0.25 mm, df=0.25 µm



Scheme 1. Formation pathway of typical products of UV-cured resin after reactive pyrolysis

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-016E

FRONTIER LAB

E-3

Problem: How can gases released from food wrap films at high temperatures be analyzed?

Analysis: Using Multi-Shot Pyrolyzer, evolved gases from various food wrap films that were exposed to 100ºC for 10min 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

Basic polymer	Organic additives labeled on the package
PVDC	Fatty acid derivatives, Epoxidized vegetable oil
PVC	Chlorinated fatty acid esters, Epoxidized vegetable oil
PE	None
PP+Nylon	Olefinic hydrocarbons, fatty acid derivatives

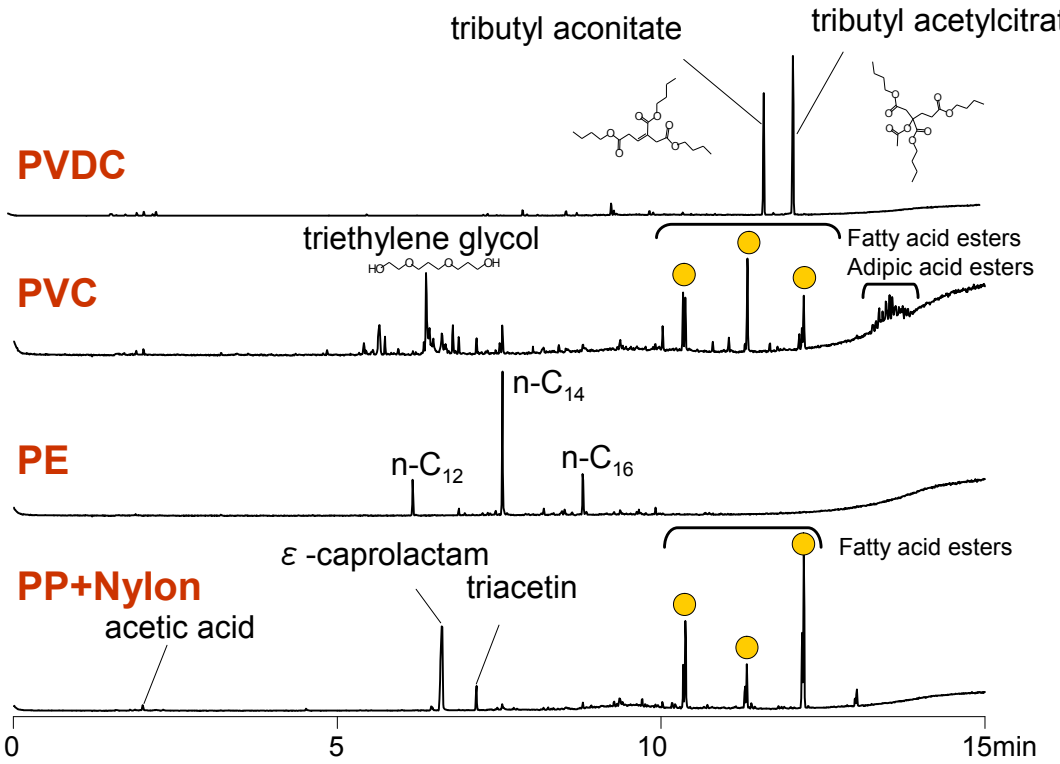


Fig. 1. Chromatograms of evolved gases from food wrap films exposed to 100ºC for 10min

Thermal desorption temp: 100ºC, Carrier gas: He, Cryo trap: 10 min, separation column: Ultra ALLOY^{+}-5, GC oven temp: 40ºC~320ºC (20ºC/min), MS scan rage: m/z=29~400

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-025E

E-4

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^2, 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.

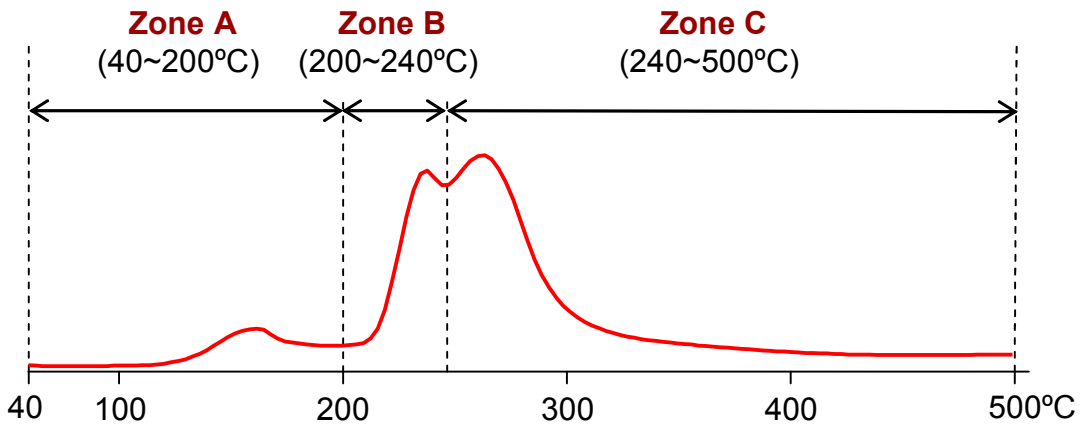


Fig. 1. Thermogram of food wrap film

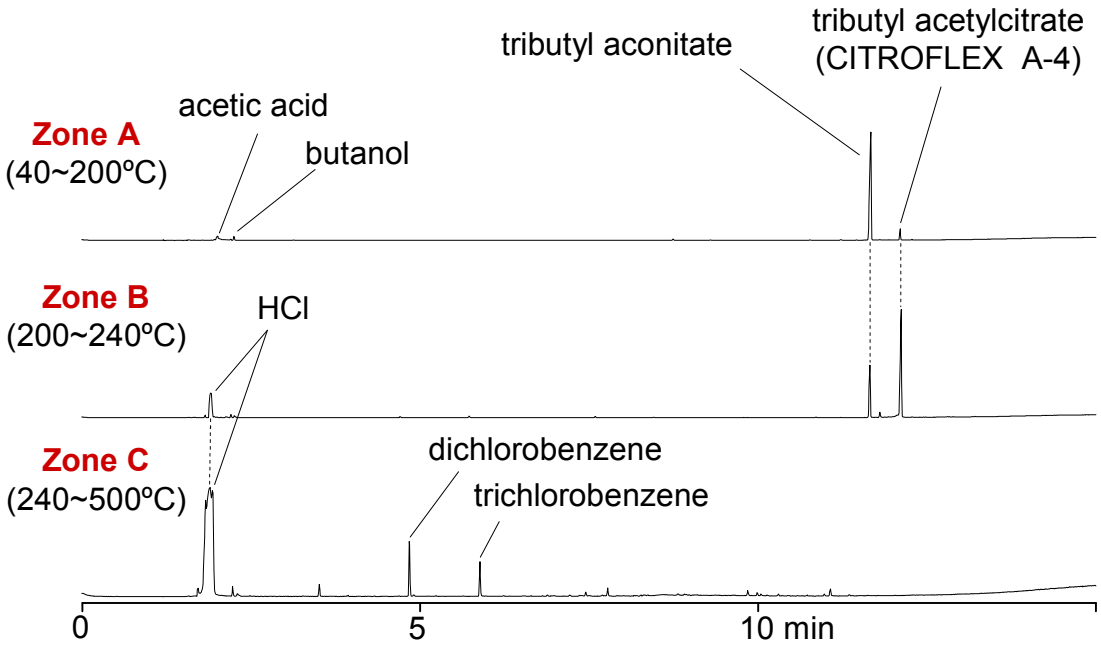


Fig. 2. Chromatograms for zones A through C by heart-cut EGA-GC/MS method

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-023E

E-5

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 Multi-Shot Pyrolyzer. Using EGA-MS technique, EGA profile is obtained by programmed pyrolysis from 40 to 600ºC at a ramp rate of 30ºC/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 C_6, C_9, C_{12}, and C_{15} derived from pyrolysis of polypropylene, and ε-caprolactam, monomer of nylon-6, were observed.

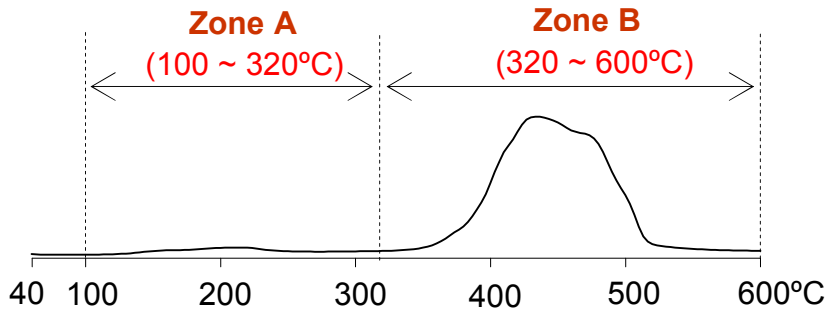


Fig. 1. EGA profile of polypropylene + nylon

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

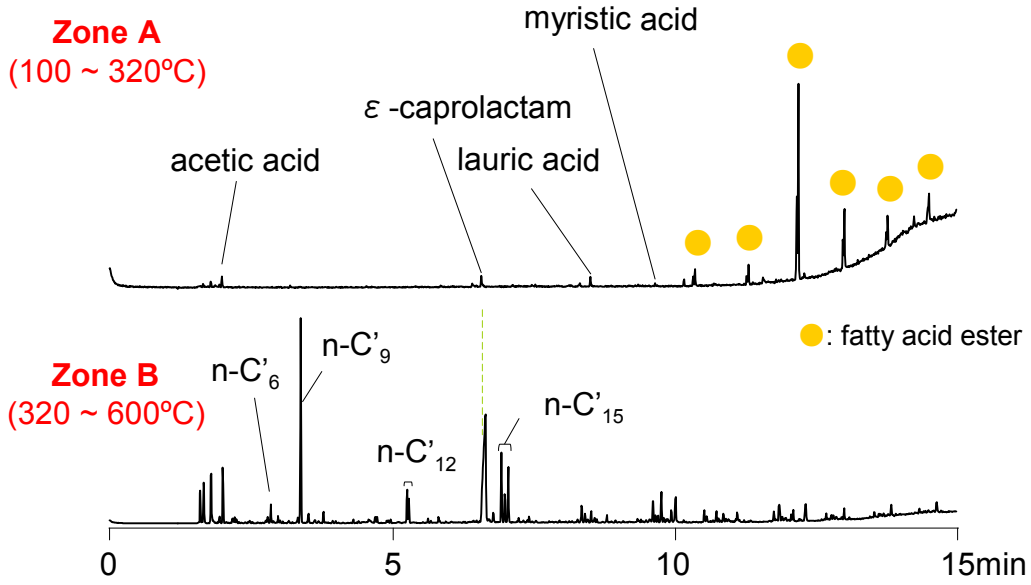


Fig. 2. Analysis results of zones A and B of polypropylene + Nylon

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

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-024E

F-1

Problem: What is the best method to quantitate additives in rubber?

Analysis: A piece of an acrylonitrile-butadiene rubber sample (NBR) weighing about 1 mg is placed in a sample cup. The sample was analyzed using EGA and thermal desorption-GC/MS.

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.

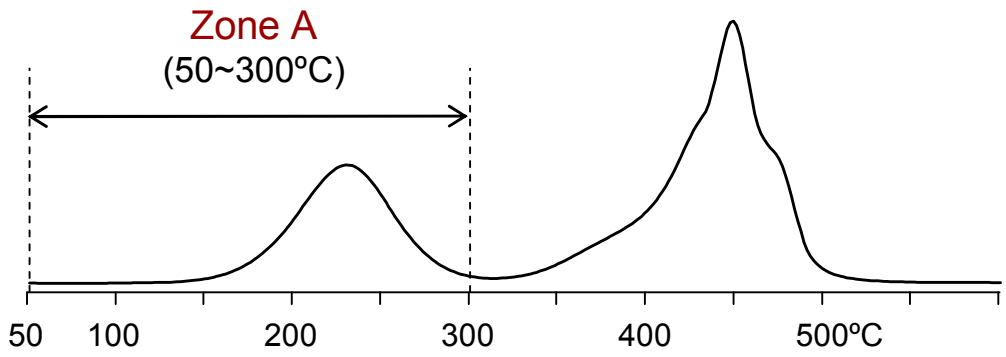


Fig. 1. EGA thermogram of NBR

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 %

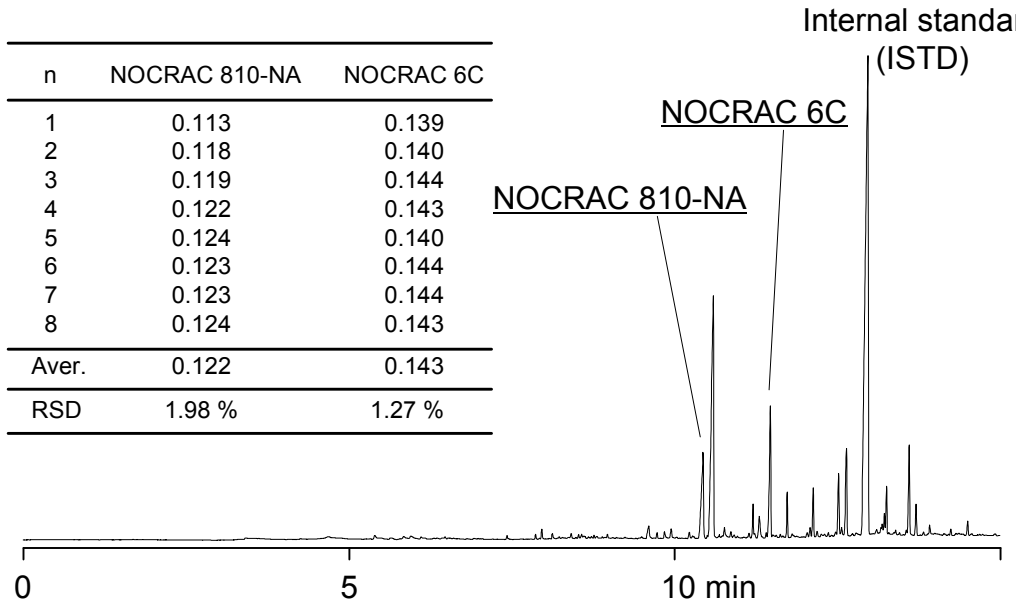


Fig. 2. Chromatogram for Zone A by (TD)-GC/MS analysis

NOCRAC810-NA: N-Phenyl-N'-isopropyl-p-phenylenediamine
NOCRAC 6C: N-Phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-005E

FRONTIER LAB

F-2

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

Analysis: A compounded rubber is analyzed by Multi-Shot pyrolyzer operating in double-shot mode, i.e., evolved gas analysis (EGA), followed by flash pyrolysis.

Result: Fig. 1 shows an EGA thermogram of a compounded rubber. Weak peaks are observed in 100~300ºC zone due to the thermal desorption of additives. In 300~500ºC zone, a broad peak due to thermal decomposition of the rubber is observed. From this result, thermal desorption was performed from 100 to 300ºC (20ºC/min), and then flash pyrolysis was done at 550ºC. 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.

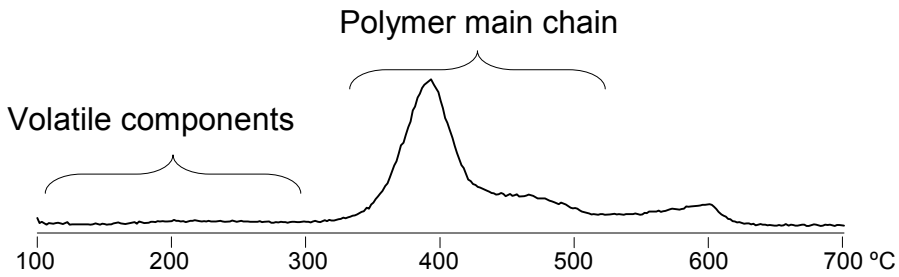


Fig. 1. Evolved gas curve of a compounded rubber

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

a. Thermal Desorption (100~300ºC, (20ºC/min)

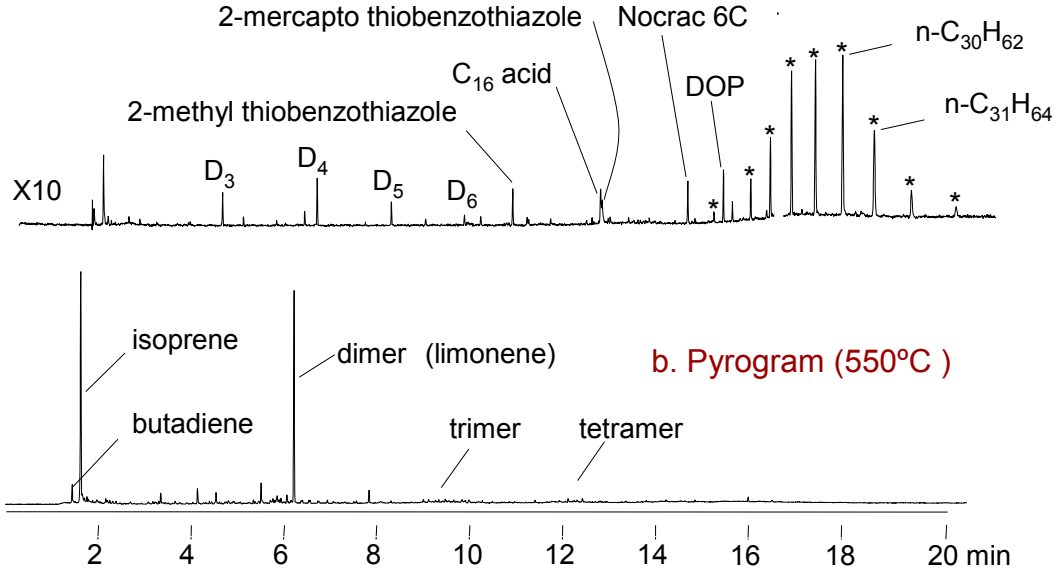


Fig. 2. GC/MS analysis of compounded rubber by double-shot technique

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

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-015E

F-3

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

Analysis: About 200 µg of a rubber mixture, composed of polybutadiene(PB)- polyisoprene (PI)-polystyrene (PS), is placed in a sample cup and pyrolyzed at 550ºC.

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.

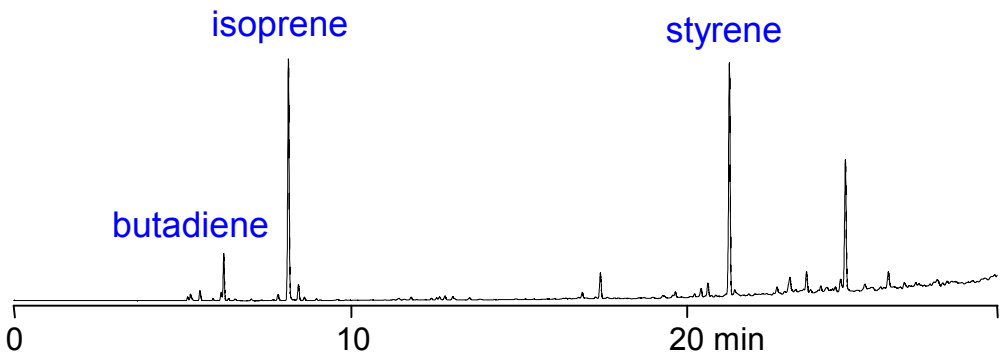


Fig. 1. Pyrogram of a blend rubber

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

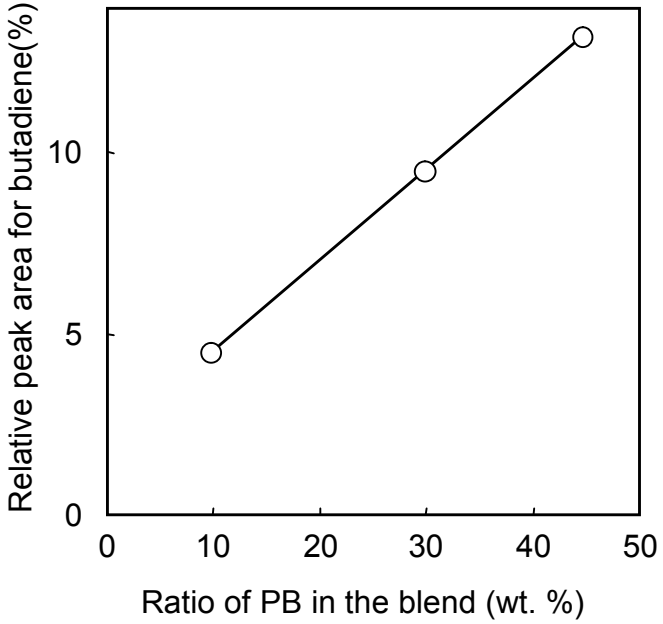


Fig. 2. Calibration curve for PB in the blend

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-047E, ISO 7270-2

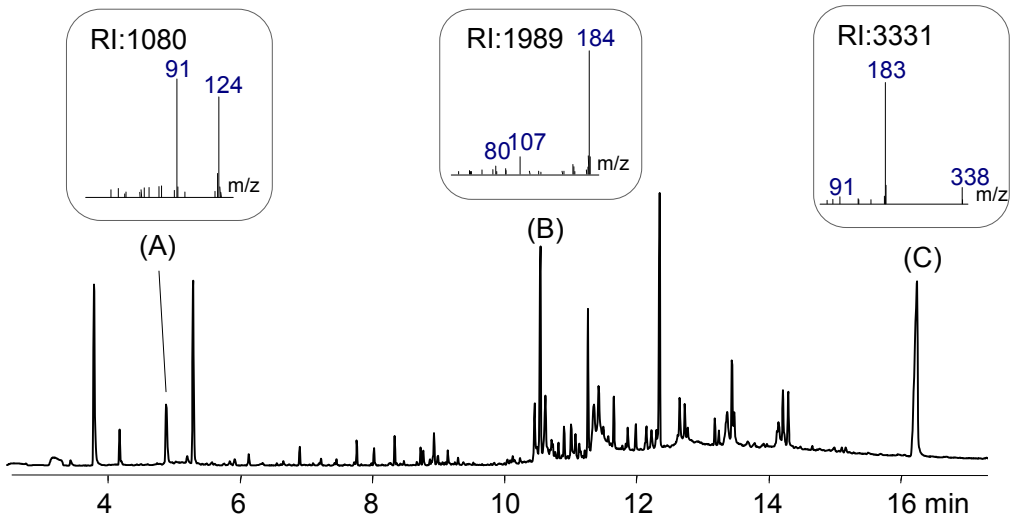
F-4

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

Analysis: 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 volatiles from an unknown rubber sample



(b) Chromatogram of *p*-(*p*-toluene sulfonylamido) diphenylamine stored in MS library

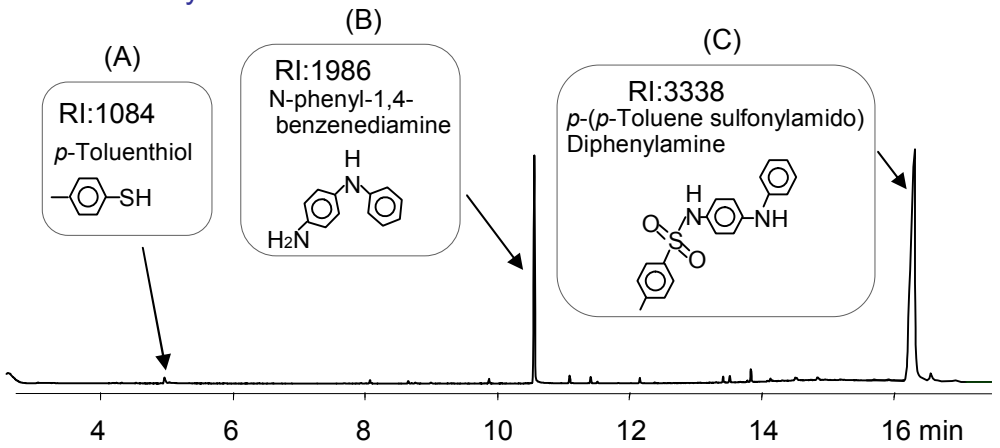


Fig. 1. Chromatogram obtained by (TD)-GC/MS technique

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-057E, ISO 10638

F-5

Problem: What analytical technique can be used to analyze a rubber of unknown components??

Analysis: The EGA-MS technique is a combination of evolved gas analysis (EGA) and mass spectroscopy (MS) using Multi-functional 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.

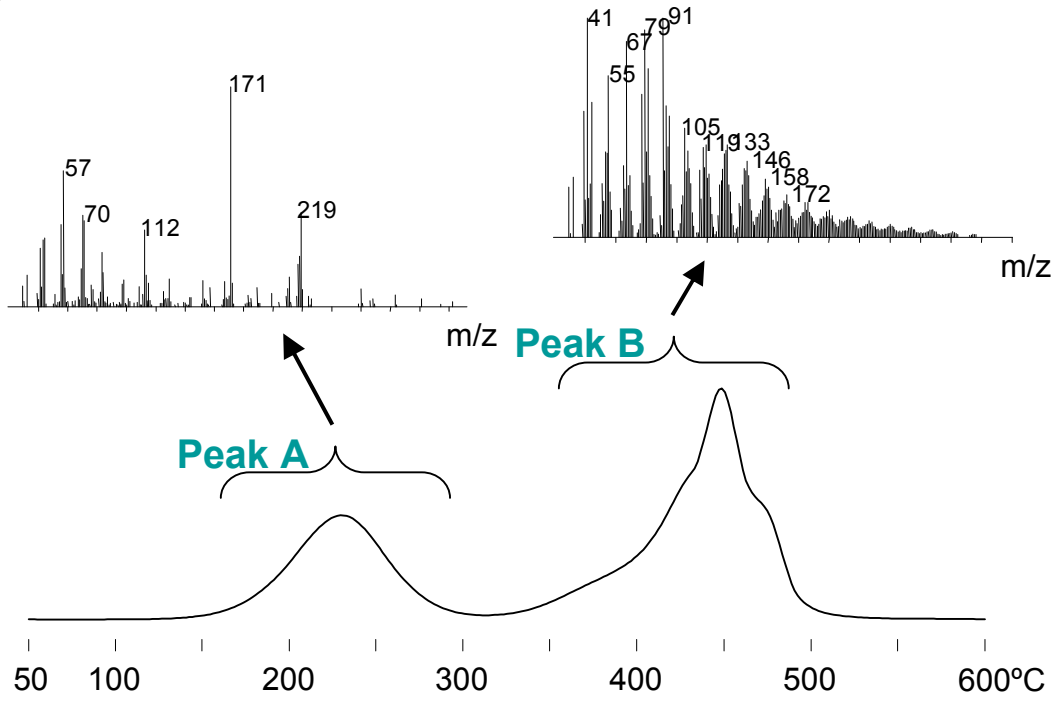


Fig. 1. EGA thermogram of a rubber and averaged Mass Spectra

Furnace temp.:50~600ºC (10ºC/min), Carrier gas : He 60ml/min, Split ratio :ca.1/50
EGA tube : id=0.15 mm, L=2.5 m (UADTM-2.5N), GC oven temp. : 300ºC
Sample :ca. 0.5 mg, MS scan range: m/z=29-400, Scan speed: 0.1 scans/sec
PY-GC interface temp.: 320ºC (AUTO mode)

Table 1. Result of library search on Peak B

Name	Match Qual
1. Polynorbornene	49
2. Polynorbornene	43
3. Acrylonitrile-butadiene rubber (NBR)*	43

* It was further analyzed by Py-GC/MS and was identified to be NBR.

Ref: Multi-functional Pyrolyzer® Technical Note, PYA3-006E

G-1

Problem: Is there an example showing the composition of adhesive?

Analysis: The EGA-MS library search is a combination of Evolved Gas Analysis, a thermal analysis technique using Multi-Shot Pyrolyzer, and mass spectrometry; and is very useful as a primary searching technique for unknowns.

Result: An example shown is analysis of an adhesive with unknown composition. Shown in Fig. 1 are the EGA curve of an adhesive and its averaged spectra obtained from zones A, B, and C with the background (BG) subtracted. Peak A was considered to arise from a low boiling component by its elution temperature, and was found to be a compound shown in Fig. 1 (a) by a normal MS library search (Wiley275). Wiley275 library search was also performed on peak B, and found mainly to be of acetic acid. Table 1 shows library search results by EGA-MS LIB with F-Search performed on peak C, and various vinyl polymers were found. Because peak B contains acetic acid, the material should contain vinyl acetate. As shown in this example, EGA-MS technique and library search with EGA-MS LIB are extremely useful as a primary library search technique.

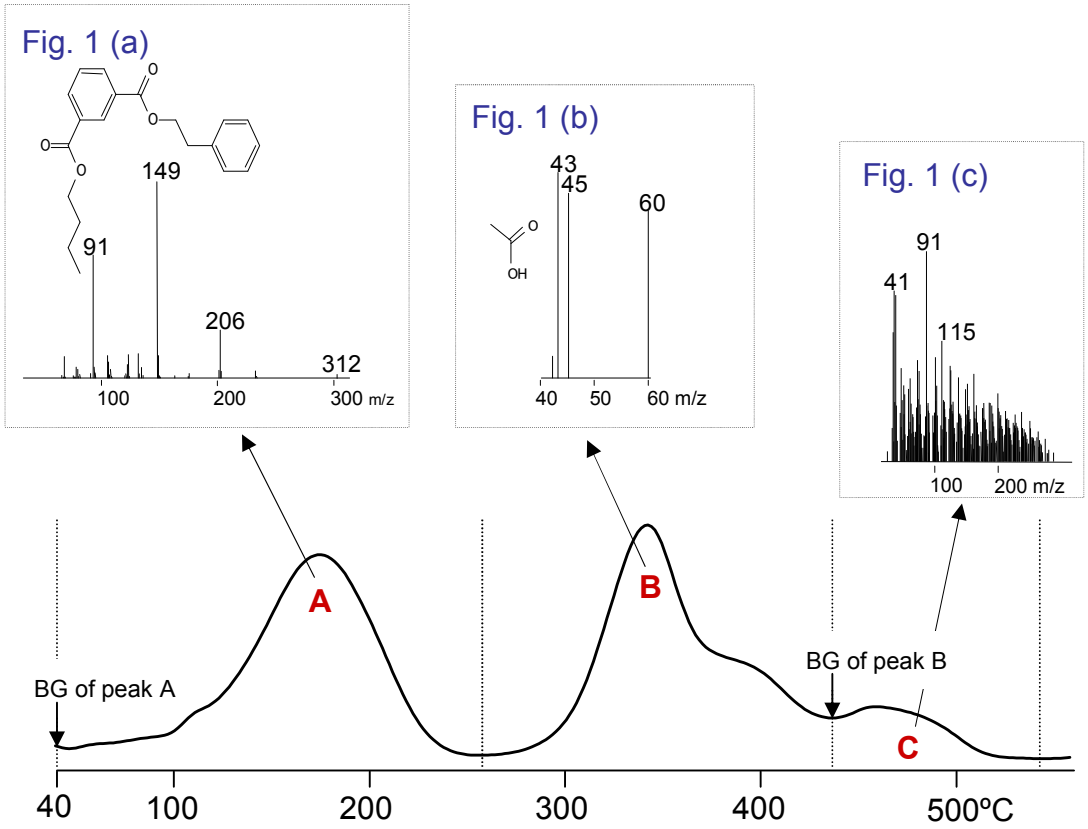


Fig. 1. EGA curve of the adhesive

Pyrolyzer furnace temp.: 100°C~600°C (20°C/min), Carrier gas: He 50kPa, Split ratio: ca. 1/50
EGA capillary tube: 0.15mm id, 2.5 m (UADTM-2.5N), GC oven temp.: 300°C isothermal
Injection temp.: 320°C, Amt. of sample : ca. 1.0mg, Detector : MS (m/z=29-400, 0.1scan/sec
PY-GC interface temp.: 320°C (AUTO mode)

Table 1. Library search result of Peak C

Name	Qual.(%)
1. Poly (vinyl chloride) ; PVC:	62
2. Poly (vinyl acetate) ; PVAc	**60**
3. Poly (vinyl alcohol) ; PVA	43

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-013E

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G-2

Problem: How can the compositional analysis of an adhesive be performed using Multi-Shot pyrolyzer?

Analysis: EGA-MS is a useful technique to determine the composition of each peak observed in the EGA thermogram. In this technique, components in each temperature zone are introduced into a GC column and temporary trapped at the front of the column using Selective Sampler and MicroJet Cryo-Trap. They are then separated and identified with GC/MS.

Result: In the EGA thermogram of an adhesive described in the previous page, three peaks, A, B, and C are observed (see Fig. 1). Fig. 2 shows chromatograms of three temperature zones obtained by GC analysis. Peak A was found to contain a phthalate ester, while peak B was found to contain acetic acid, butyl acetate, and butyl acrylate. Acetic acid is considered to arise from polyvinyl acetate (PVAc), and butyl acrylate from thermal decomposition of polybutyl acrylate. Peak C contained a variety of aromatic compounds derived from thermal decomposition of polyene structure of the polymer backbone.

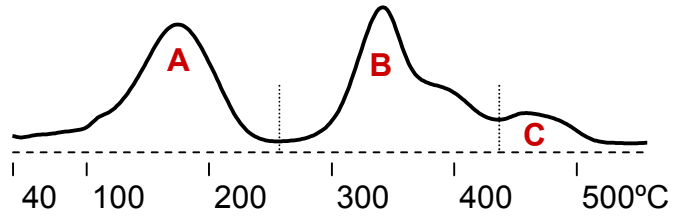

Fig. 1. EGA Curve of an adhesive

See the previous page for analytical conditions

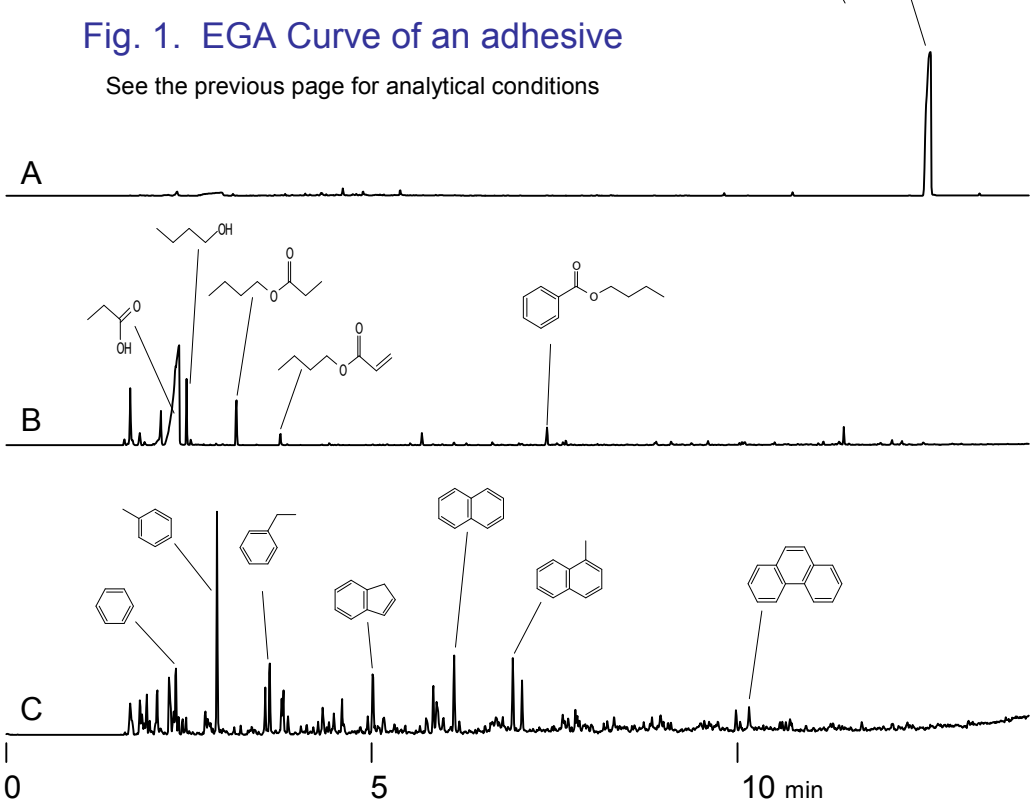

Fig. 2. Chromatograms of temperature zones of EGA thermogram

Pyrolysis temp.: 40ºC~600ºC (20ºC/min), Column flow rate: 1ml/min, Split ratio: 1/50
Separation column : Ultra ALLOY+-5 (5% diphenyl polysiloxane), 30m, 0.25mm id, df=0.25µm
GC oven temp.: 40ºC~320ºC (20ºC/min), Sample: 0.8mg, Detector: MS (m/z=29-400, 2scans/sec)

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-014E

G-3

Problem: Has the curing process of epoxy resin been studied using Py-GC technique?

Analysis: Samples of a diglycidyl ether of bis-phenol A (DGEBA, Mn≈340) prepolymer with various amounts of 1-Benzyl-2-Methyl Imidazole (1B2MZ) were cured at 180°C for 3 hours and were analyzed by Py-GC at 590°C.

Result: Figure 1 shows typical pyrograms of DGEBA cured with various amounts of 1B2MZ at 180°C for 3 hrs. Relationships between intensities of observed peaks and the amounts of catalysts added are shown in Figure 2. It was found that the yields of the pyrolyzates with epoxide groups decreased with increase of the degree of cure, while those of various phenols, characteristic of prepolymer skeleton increased. The results observed corresponded well to the those deduced from Tg measurements by DSC.

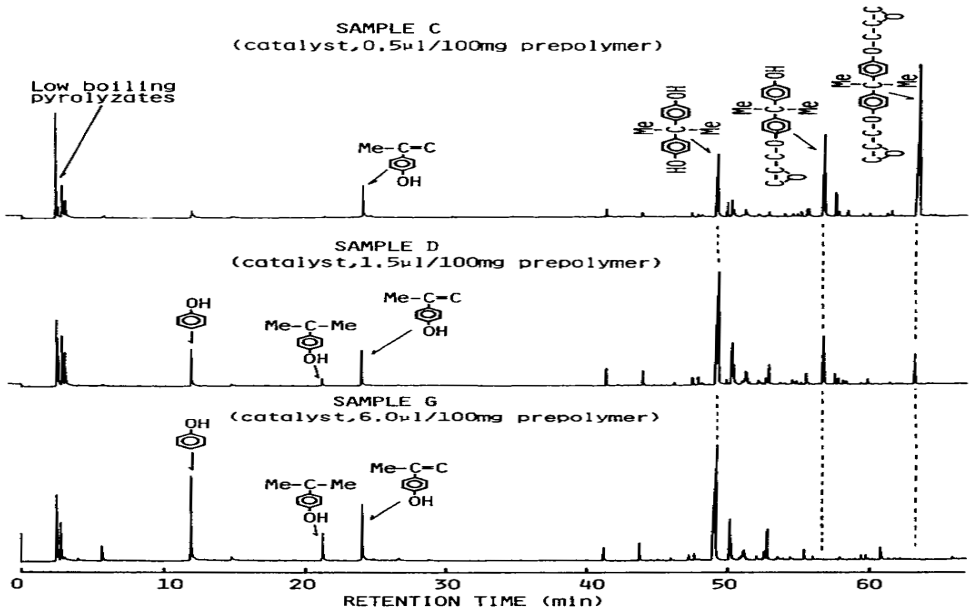

Fig. 1. High-resolution pyrograms of epoxy resins cured with various amounts of imidazole catalyst at 180ºC for 3h.

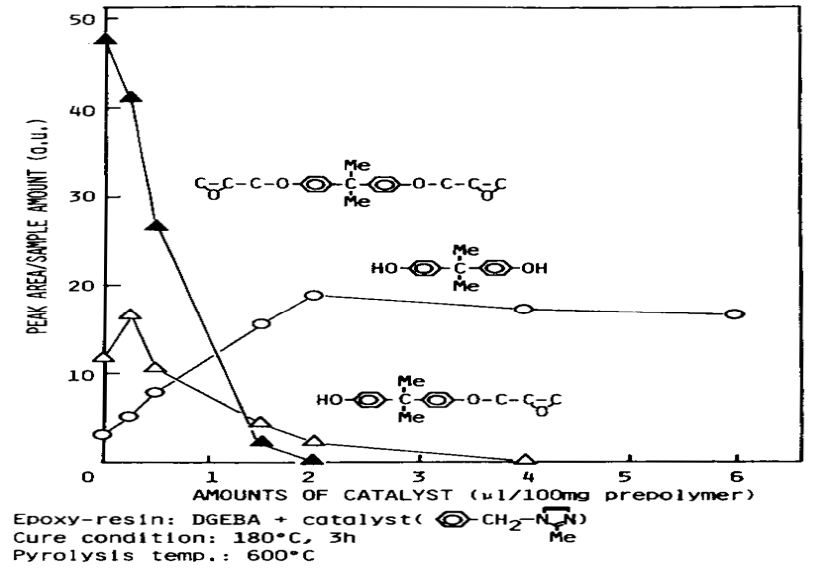

Fig. 2. Changes of characteristic products from epoxy resins as a function of catalyst amount.

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-034E

FRONTIER LAB

H-1

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

Analysis: EGA-MS method is one of the simple thermal analysis methods using a multi-shot pyrolyzer, and is the primary analysis method for unknown sample.

Result: Fig. 1 shows the thermogram of a printer toner and 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/EGA library search is a very powerful set of 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

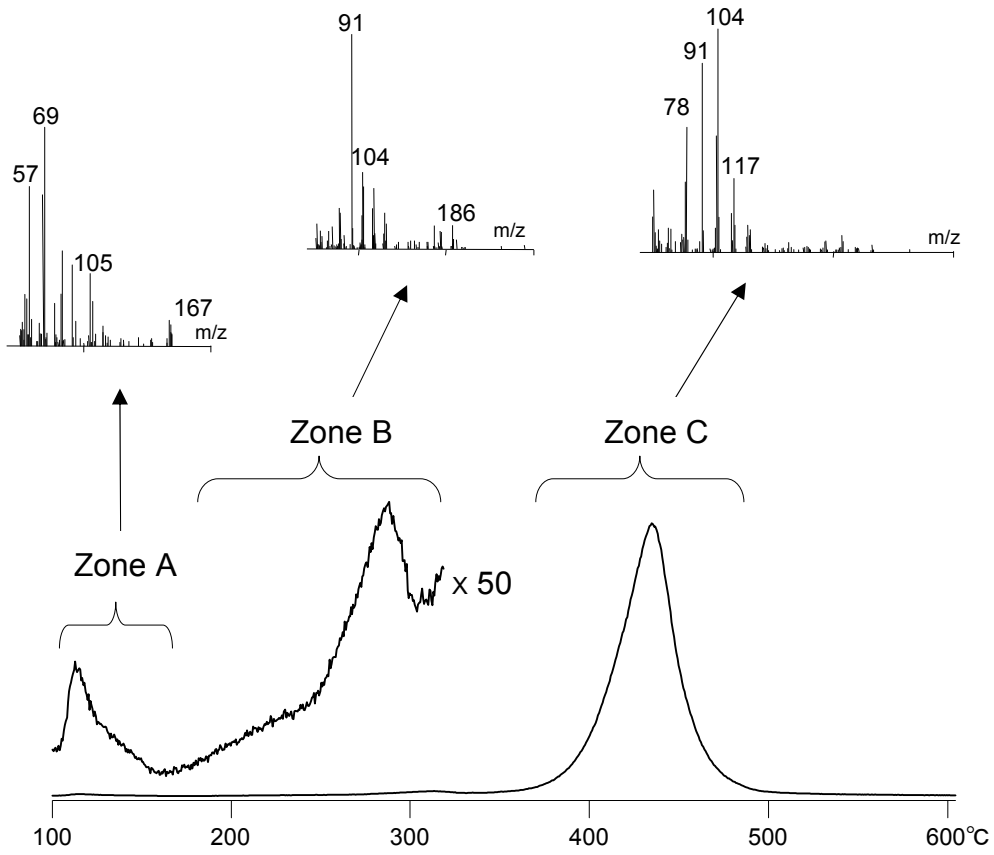

Fig. 1. EGA thermogram of a printer toner and mass spectra of 3 temperature zones

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

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-018E

H-2

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 Multi-Shot Pyrolyzer is used?

Analysis: Selective Sampler and MicroJet Cryo-Trap 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.

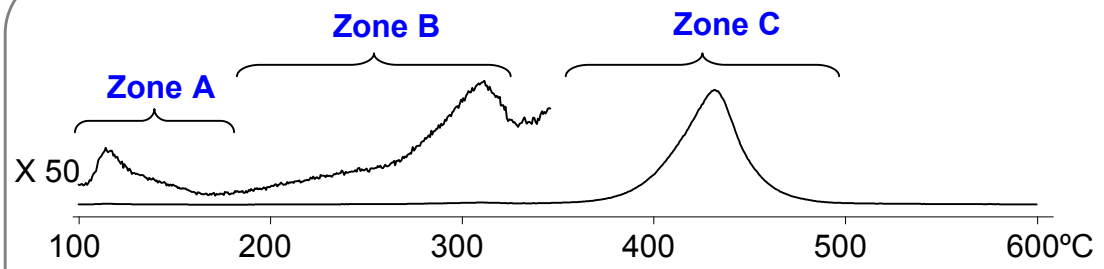

Fig. 1. EGA thermogram of a printer toner

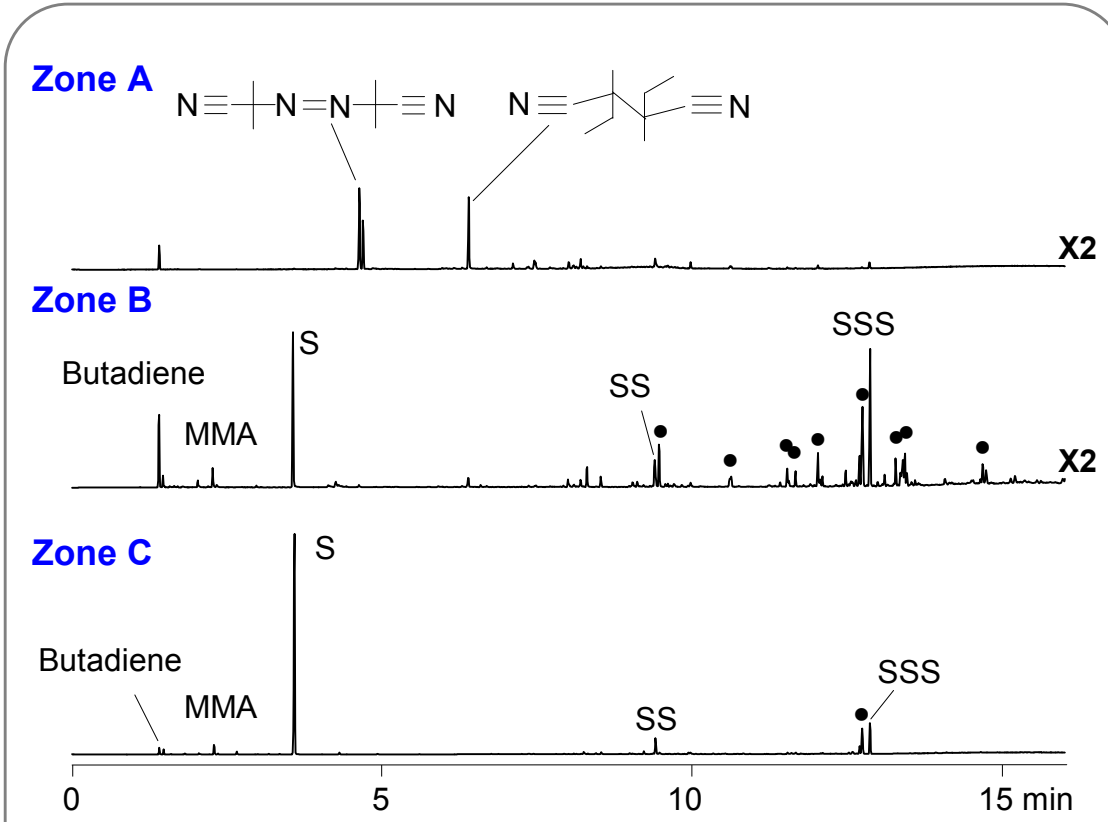

Fig. 2. Chromatogram of each temperature zone of EGA profile

Separation column : Ultra ALLOY⁺-5 30M-0.25F
GC oven temperature : 40ºC~20ºC/min~320ºC (2min hold)

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-019E

FRONTIER LAB

I-1

Problem: How can additives in paper (e.g. alkylketene dimer, AKD) be analyzed without solvent-extracting them?

Analysis: They can be analyzed by pyrolysis gas chromatography (Py-GC). Shown here is an example in which AKD used a sizing agent is analyzed by flash pyrolysis technique.

Result: AKD exists in paper as in three forms: unreacted AKDs, ketones upon hydrolysis, and ones bonded to cellulose via hydroxyl group. Using flash pyrolysis technique, AKD is detected as dialkylketone upon hydrolysis as shown in Fig. 1. Shown in Fig. 2 is a pyrogram of an AKD-added paper obtained by flash pyrolysis. Three dialkylketones originated from AKD were detected within eight minutes. As shown here, the use of Py-GC technique eliminates pre-treatments and allows for rapid analysis of AKD.

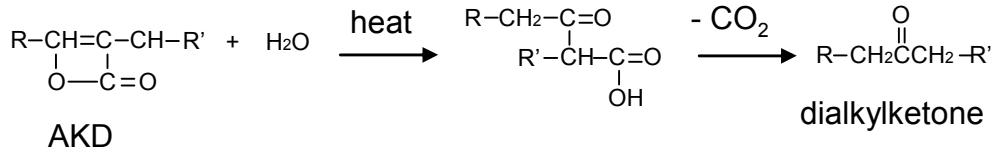

Fig. 1. Formation of ketone by hydrolysis of AKD

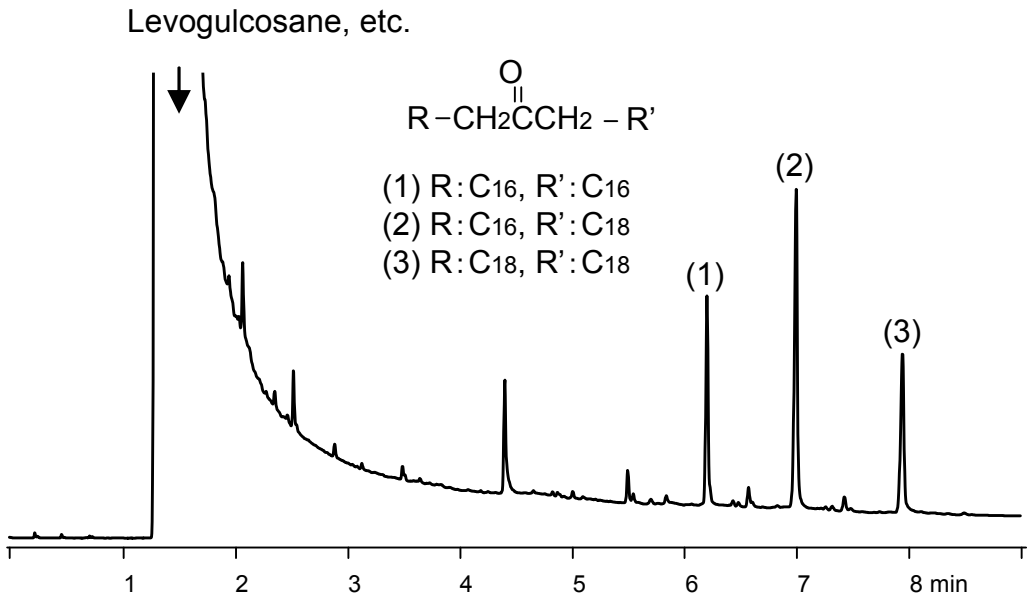

Fig. 2. Analysis of AKD in paper by flash pyrolysis

Pyrolysis temp.: 600ºC, carrier gas: He, split ratio: 1/50
Separation column: Ultra ALLOY+-1, 30M-0.25F
GC oven temp.: 225ºC - 20ºC/min - 330ºC, injector temp.: 320ºC
Sample: 2 mg, detector: FID

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-007E

I-2

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 46ºC with 60±5% relative humidity for 52 days. About 200 µg of silk sample was pyrolyzed at 600ºC 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.

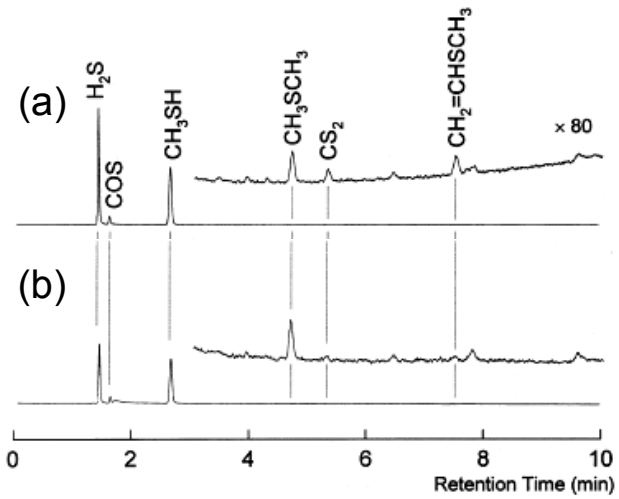

Fig. 1. Pyrograms of photo degraded silk samples at 600ºC observed by SCD: (a) not exposed and (b) exposed for 52 days

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[a*]	14.8±2.9 (0.22)	10.6±2.0 (0.16)
Cys[b*]	14.6±0.8 (0.18)	7.0±0.2 (0.08)
Cys-Cys[c*]	1.48±0.19 (0.036)	0.54±0.23 (0.013)

a* from peak intensity of CH_3SH

b* from peak intensity of H_2S

c* from peak intensity of CS_2

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-046E

J-1

Problem: Is there an example of pyrolysis in which a sample is pyrolyzed both in helium and in air? If so, how is that compared?

Analysis: It is often instructive to compare the pyrogram of a material pyrolyzed in an inert atmosphere (He) with one obtained in an oxidative atmosphere (air). Here, the pyrolysis of tobacco was performed and pyrolyzates were examined.

Result: Pyrograms were obtained in air and He at 600 and 800ºC using PY-GC/MS. See Fig. 1 for analysis conditions. The peak identifications are based upon MS data. There are significant differences between the left (He) and right (air) pyrograms. Nicotine found in He at 600ºC is thermally decomposed to nicotinonitrile, and the peak for acetic acid is greatly reduced at 800ºC. In an oxidative atmosphere, nicotine is degraded to 3-vinylpyridine and the formation of benzene is evident at 800ºC.

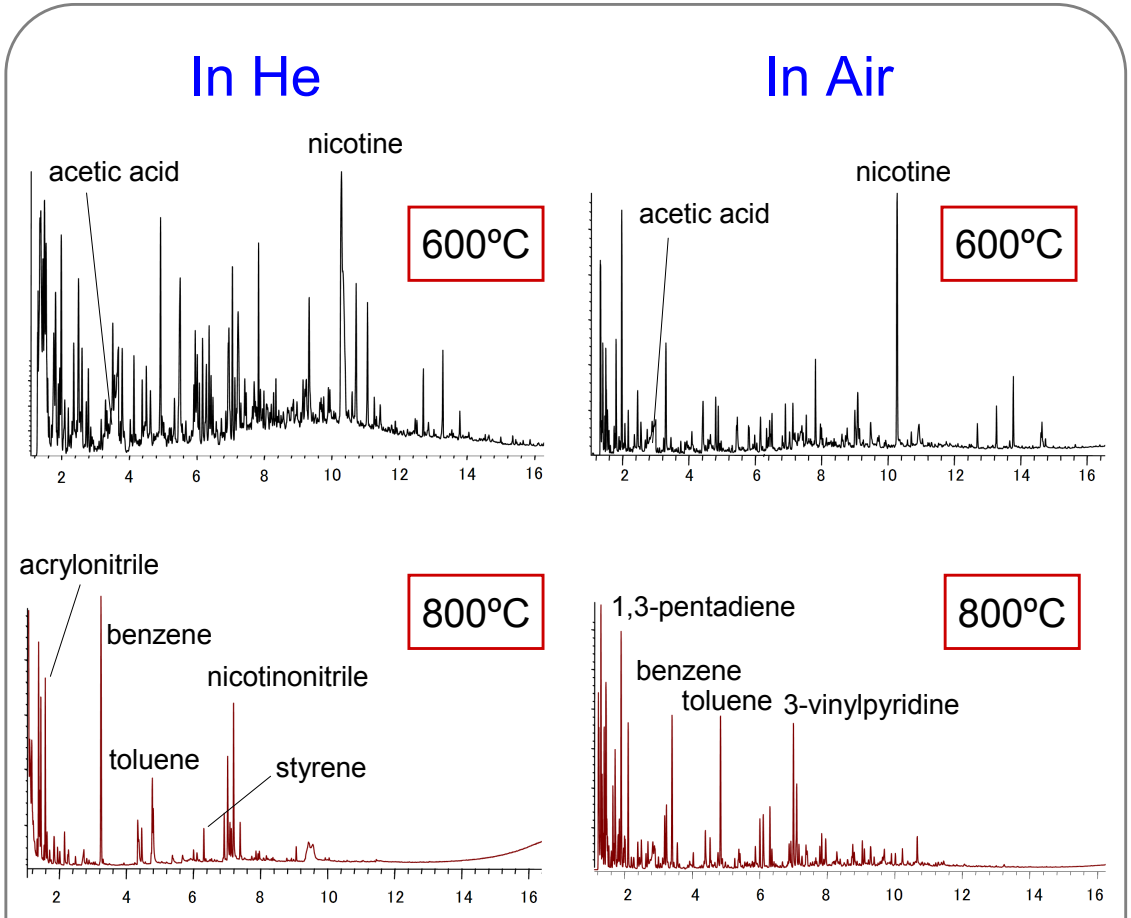

Fig. 1. Pyrograms of tobacco obtained at 600ºC and 800ºC in air and in helium

Pyrolyzer temperature: 600/800ºC, GC injection port: 320ºC, GC oven : 40(2 min hold)-320ºC (20ºC/min), Separation column : Ultra ALLOY-1 30m x 0.25mm i.d., 0.5µm film, Column flow :1.0 mL/min, Split ratio: 1/50, Sample wt.: ca 0.5 mg, Other devices : Carrier Gas Selector, Selective Sampler, MicroJet Cryo-Trap

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-062E

J-2

Problem: How can the analysis of the surface active agent in mineral oil be done using the Multi-Shot pyrolyzer?

Analysis: A mineral oil: Hygold 100 contains about 500 ppm of sodium di(2-ethylhexyl)sulfosuccinate (DESS) as a surface active agent. The Multi-Shot pyrolyzer was used with the Heart-cut EGA-GC/MS technique.

Result: As the EGA thermograms shown in Fig. 1, the hydrocarbons evolve between 100-180ºC. DESS decomposes between 180-270ºC to give di(2-ethylhexyl)fumarate (DEF). When a Hygold 100 sample containing 500 ppm of DESS was analyzed by thermal desorption GC/MS without heart-cutting, the DEF peak co-eluted with the hydrocarbons as shown in Fig. 2-a. The impact of the interfering compounds on the DEF determination was reduced by heart-cutting the temperature zone over which DEF is formed. The result obtained by heart-cutting the 160-300ºC zone (Fig. 1) is shown in Fig. 2-b. Interference with the DEF peak was almost eliminated. DFE could be clearly observed with the reproducibility of 4.7 %RSD (n=5).

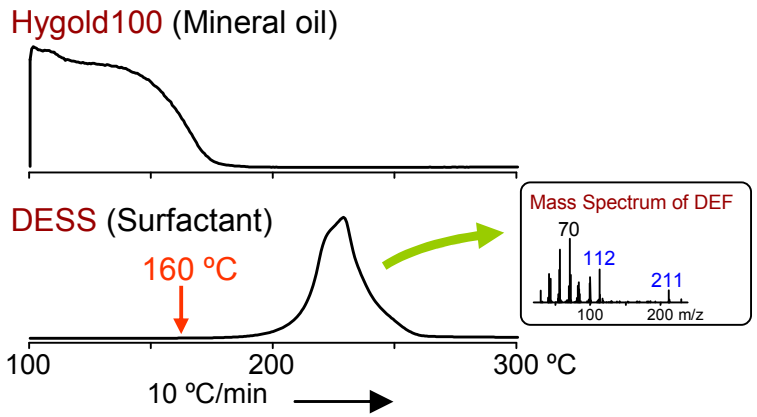

Fig. 1. EGA thermograms of DESS and Hygold100

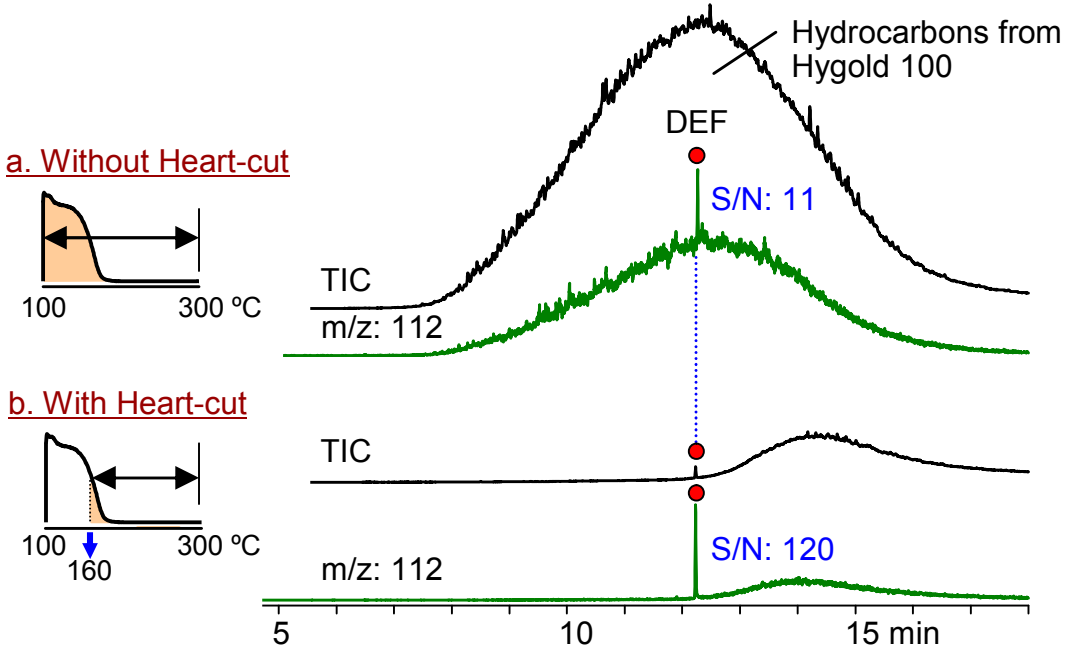

Fig. 2. Quantitative analysis of DESS (500 ppm) contained in Hygold100 using Heart cut–GC/MS

Pyrolysis temp.: 100 – 300 ºC (10 ºC/min), GC oven temp.: 40 – 320 ºC (20 ºC/min, 4 min)
Separation column: Ultra ALLOY^{+}-5 (L=30 m, i.d.=0.25 mm, df = 0.25 µm),

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-070E

J-3

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 C16-C18 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 C16-C18 aliphatic acids and flavonoids showed a large difference.

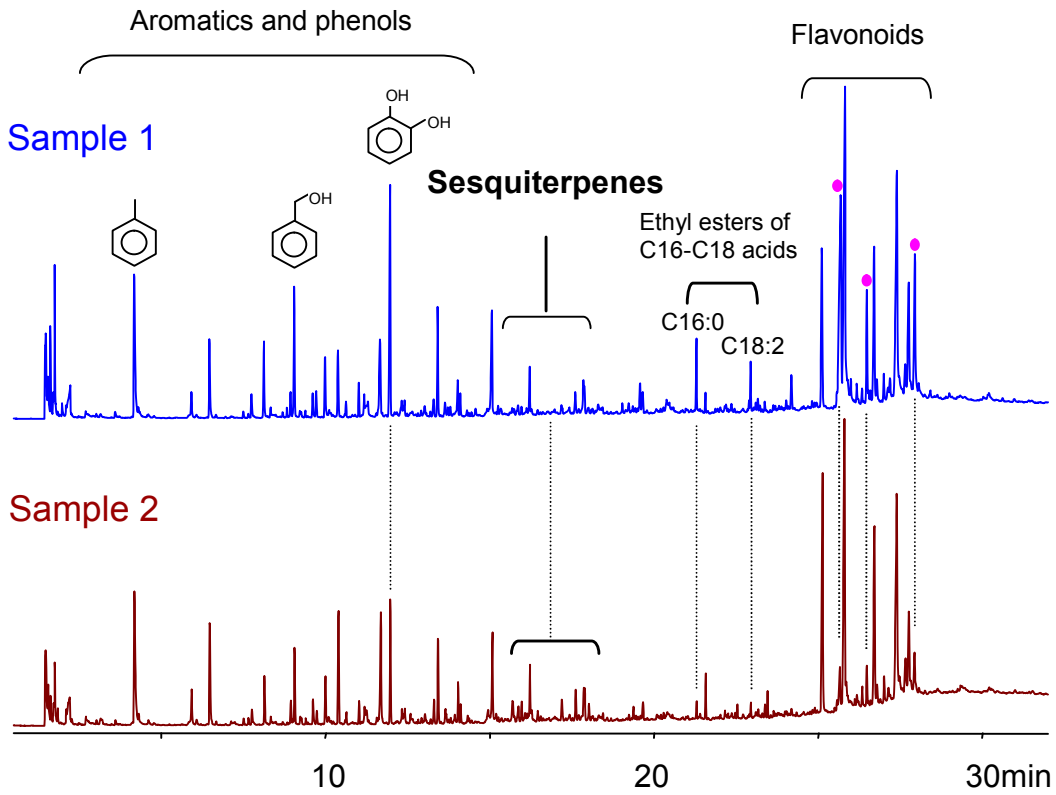

Fig. 1. TIC pyrograms of two different propolis samples

Multi-Shot Pyrolyzer: EGA/PY-3030D
Pyrolysis temperature: 550ºC, 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: 40ºC~300ºC (10ºC/min), Sample: 300 µg, Detector: MS (m/z: 29-550, 2 scans/sec)

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-030E

K-1

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.

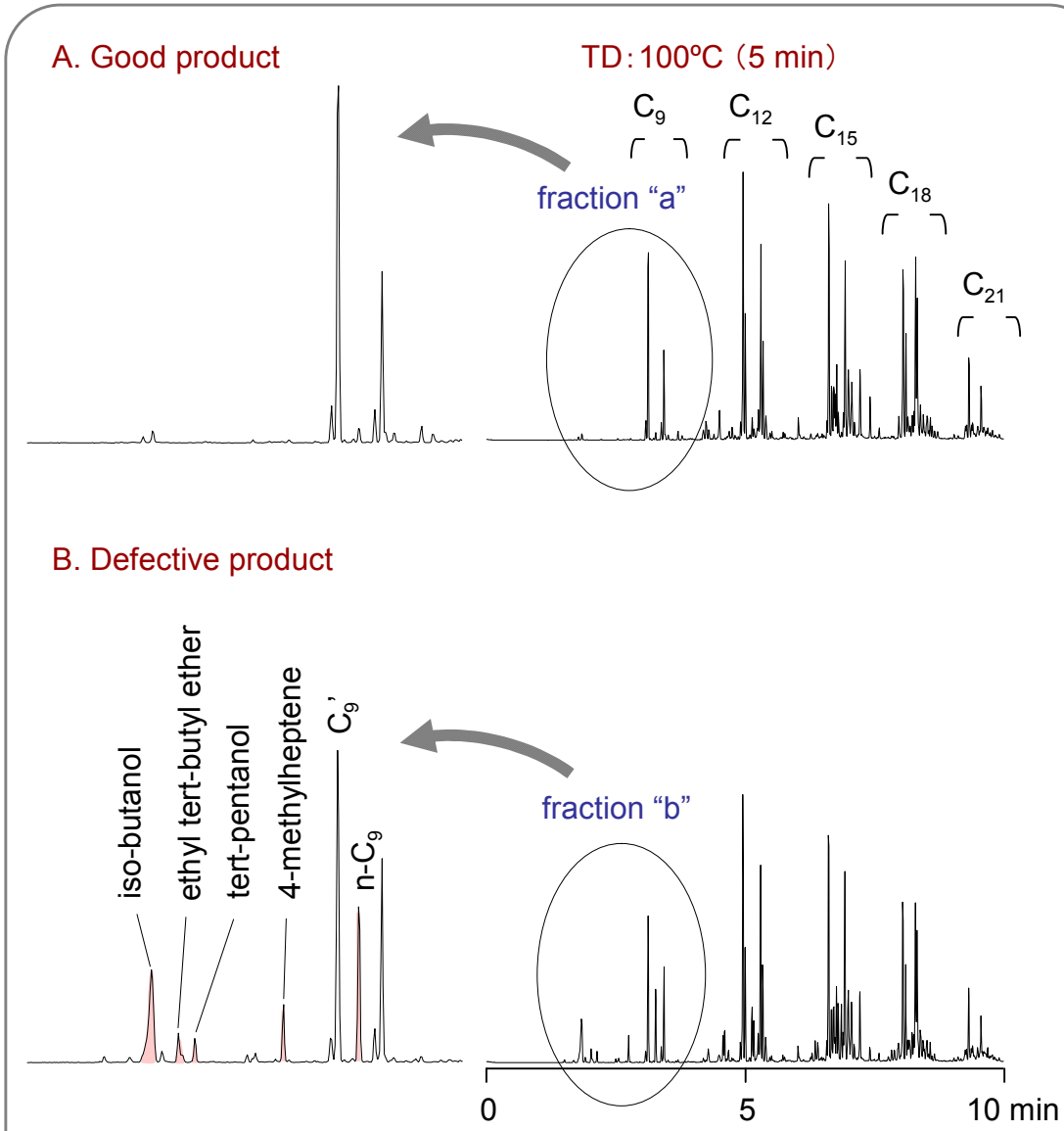

Fig. 1. Chromatograms of “good” and “defective” PP samples by (TD)-GC/MS analysis

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-006E

FRONTIER LAB

K-2

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 400~500ºC was found to be a polystyrene by F-Search with polymer library. The average mass spectrum for the weak peak observed at 250~350ºC 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 200~400ºC (20ºC/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%.

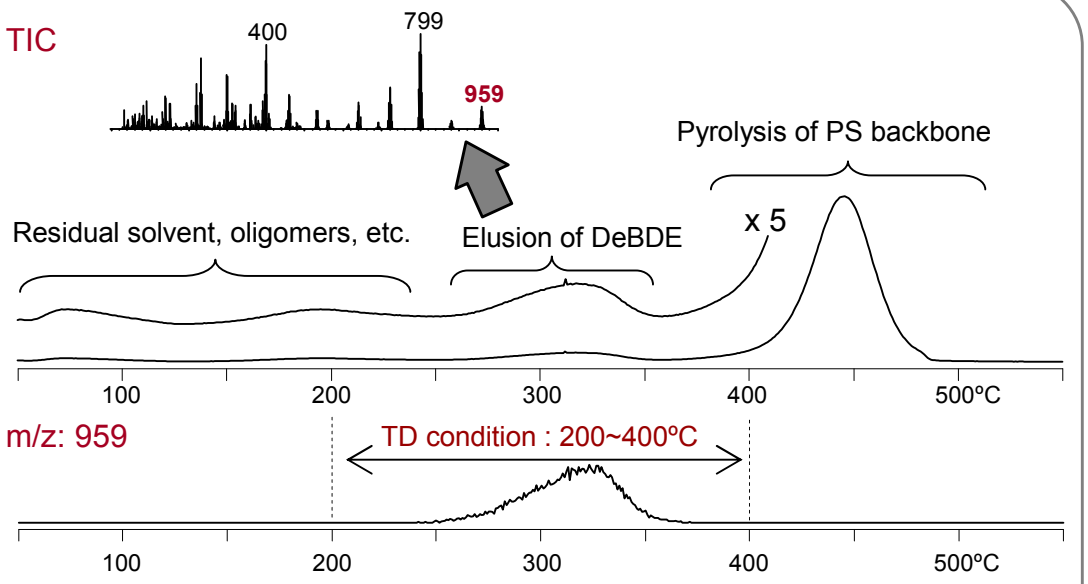

Fig. 1. EGA thermogram of waste plastic

	Peak area for DeBDE (x 10^6, m/z: 800)
1	17.05
2	18.15
3	18.78
4	19.07
5	18.30
Average	18.27
RSD (n=5)	3.5 %

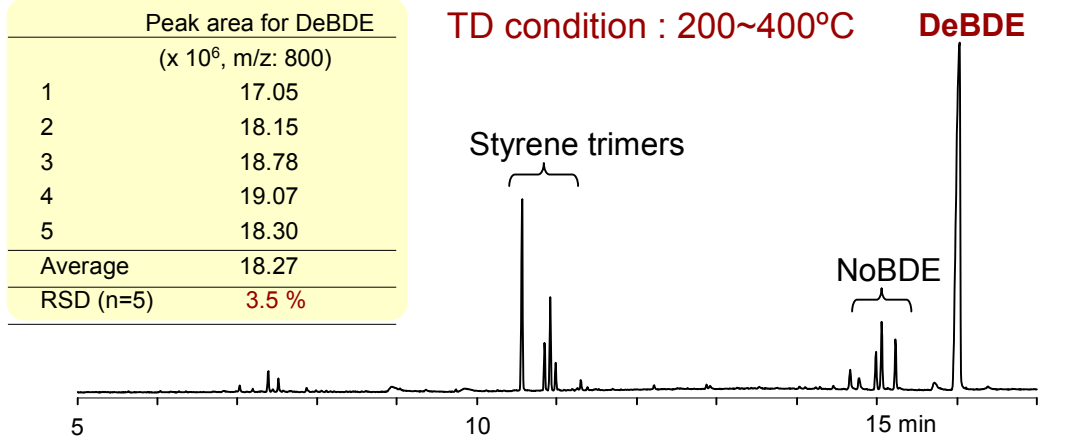

Fig. 2. Chromatogram of waste plastic obtained by (TD)-GC/MS
Separation column : UA-PBDE 15M-0.05F (Frontier Lab)
Thermal desorption temp. : 200ºC~20ºC/min - 400ºC

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-052E

FRONTIER LAB

K-3

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 600ºC, 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.

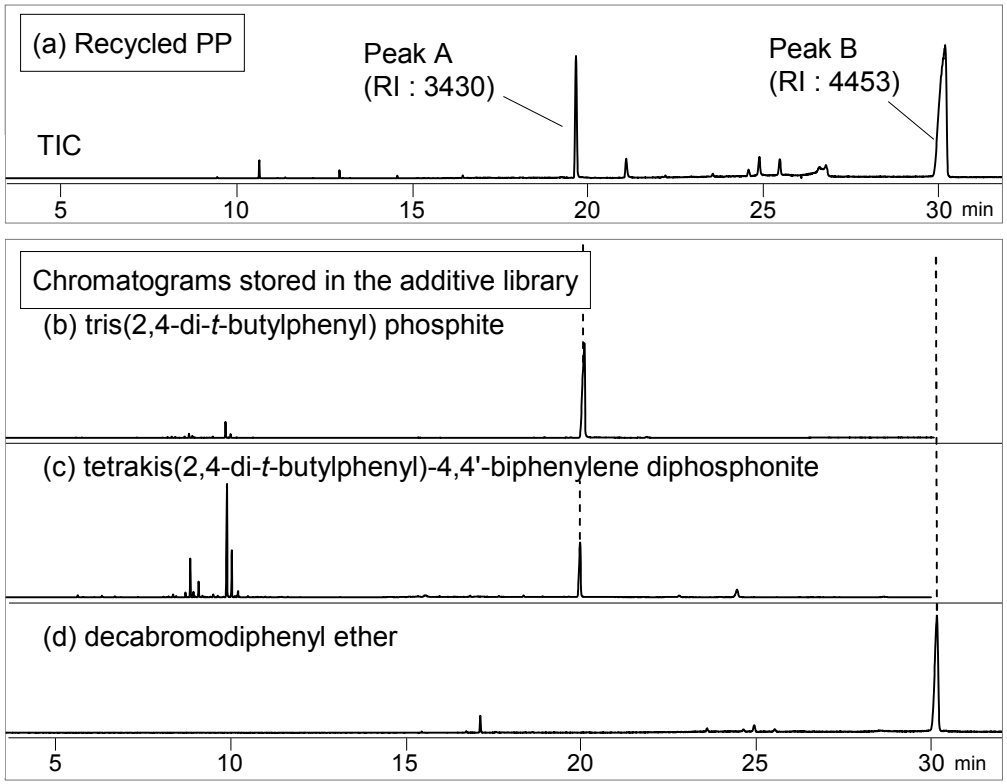

Fig. 1. Chromatograms of PP, and additives stored in MS library

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

Table 1. Additive MS library search results

	Candidates compounds	Match quality[%]	RI
Peak A RI:3430	**1. tris(2,4-di-*t*-butylphenyl) phosphite**	**62**	**3451**
	2. 2,4,8,10-tetra-*t*-butyl-5,7-dioxa-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. decabromodiphenyl ether**	**89**	**4412**
	2. isomer of bromophenyl heptabromodiphenyl ether	13	3738
	3. tetrabromo phthalimide	5	2814

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-054E

K-4

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 fragmentgram for the six restricted phthalates, the temperature range in which all phthalates were thermally desorbed was determined to be 100 to 350ºC.

Table 1 Use 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)

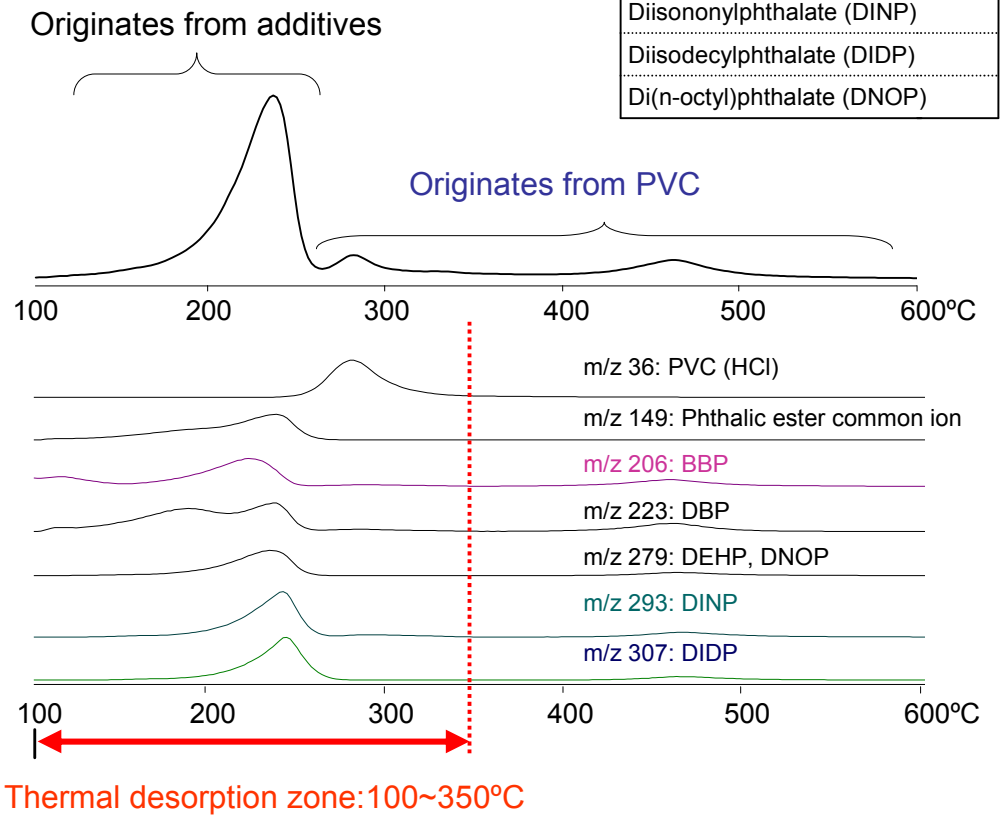

Fig. 1. TIC thermogram and extracted mass chromatograms of PVC, to which 1% each of phthalate was added

Pyrolyzer furnace temp.: 100 – 600ºC (20ºC/min), GC oven temp.: 300ºC
EGA tube: UADTM-2.5N (L=2.5 m, i.d.=0.15 mm), column flow rate: 1 ml/min He, split ratio: 1/20, injector temp.: 320ºC

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-063E

K-5

Problem: When phthalates in plastic toys are analyzed using thermal desorption (TD)-GC/MS, does the sample form influence the reproducibility?

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 100-350ºC. 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 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)

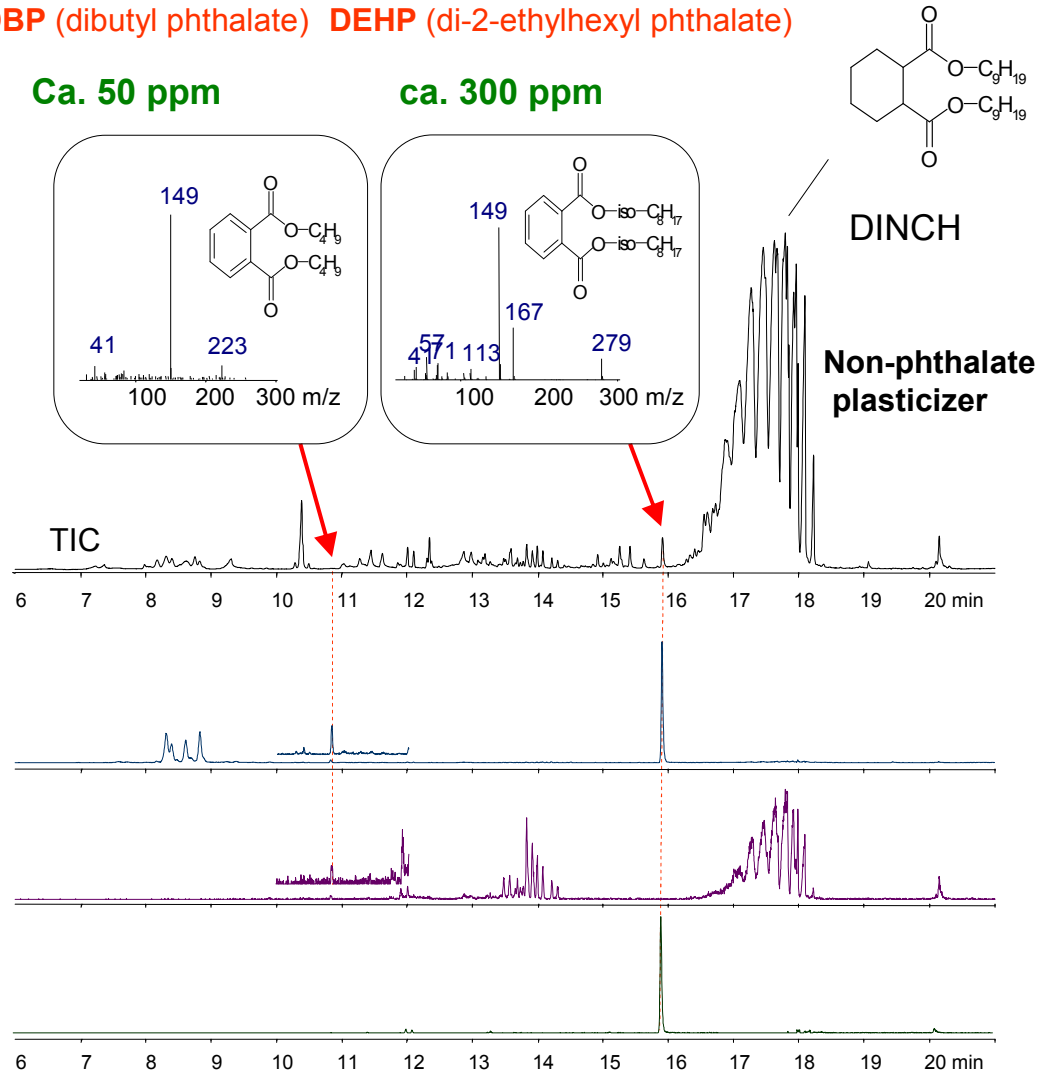

Fig. 1. TIC and extracted ion chromatograms of a PVC sample obtained by (TD)-GC/MS

Thermal desorption temp: 100 - 350ºC (40ºC/min, 3 min)
GC oven temp: 80 - 320ºC (10ºC /min, 6 min)
Separation column: Ultra ALLOY⁺-1 30M-0.25F

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-064E

L-1

Problem: Have volatiles released from a UV curable resin been analyzed using UV/Py-GC/MS?

Analysis: A dry film of an acrylic UV curable resin was analyzed by ultraviolet light (UV) irradiation/ pyrolysis-GC/MS technique. A small disc-shaped sample (3 mm in dia., 350 µg) was used. The UV irradiation was conducted in He atmosphere at 60ºC for 10 min using a micro UV irradiator (UV-1047Xe) which uses a Xe lamp as a light source.

Result: Chromatograms of volatile components released from the resin with and without UV irradiation and their magnified view are shown in Fig. 1. Without UV irradiation, decomposed polymerization initiator was only observed, on the other hand, upon UV irradiation various organic compounds including 300 ppm of methyl methacrylate (MMA) against the original sample weight were observed. As shown here, the UV/Py-GC/MS technique allows you to analyze volatiles released from a UV curable resin during its curing process without complicated treatments.

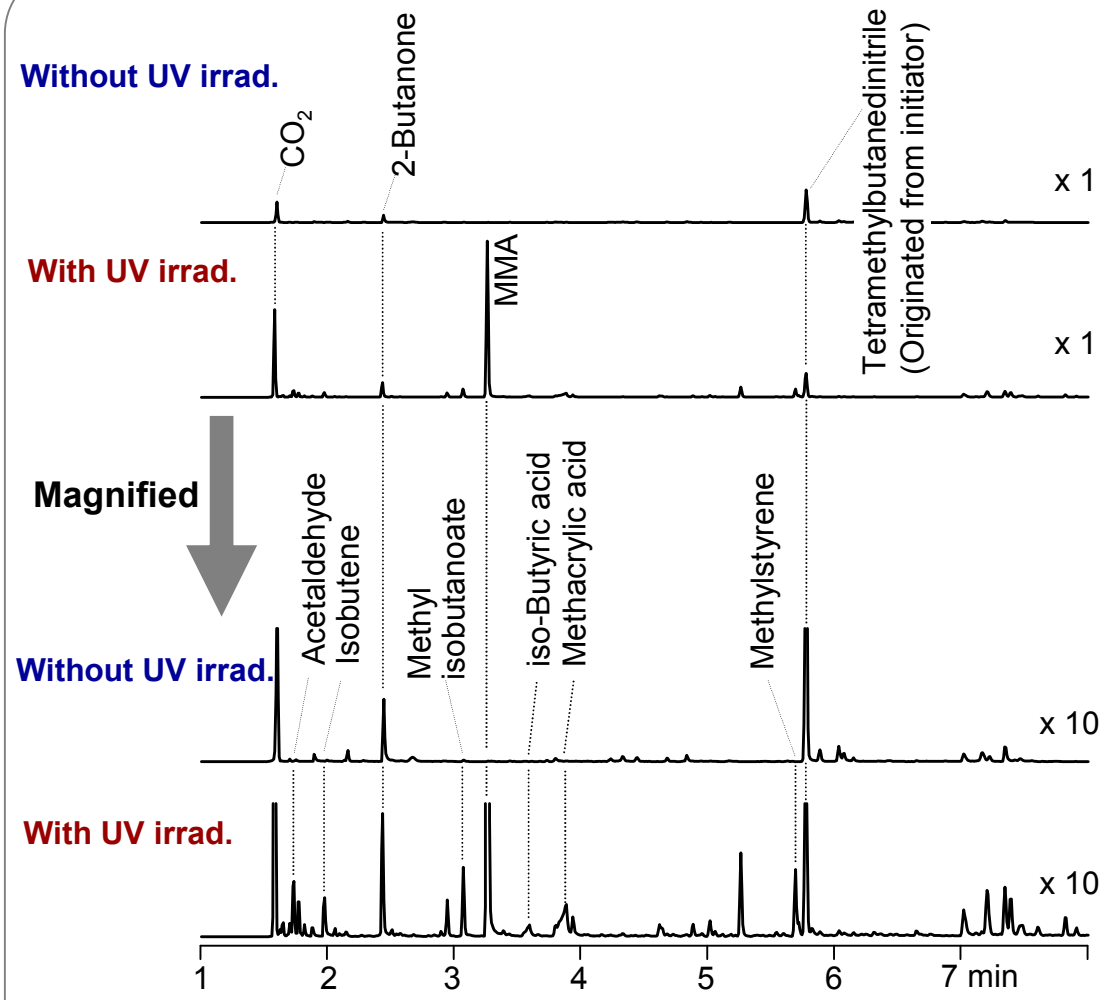

Fig. 1. Analysis of volatiles released from UV curable acrylic dry film

Micro UV irradiator: UV-1047Xe,
separation column: Ultra ALLOY+-1 (dimetylpolysiloxane), L=30 m, id=0.25 mm, df=0.5 µm,
atmosphere gas: He, Column flow rate: 1 ml/min, split ratio: 1/10,
sample size: 350 µg (3 mm diameter disc), GC oven temp: 40 ~ 300 ºC (20 ºC/min)

Ref: Multi-functional Pyrolyzer® Technical Note, PYA5-001E

L-2

Problem: Has the photo/thermal/oxidative degradation of polycarbonate (PC) been studied? If so, please describe.

Analysis: The photo/thermal/oxidative degradation of PC was examined using a UV irradiation/ pyrolysis (UV/Py)-GC/MS. The UV irradiation of the sample was performed at 100ºC in air for 1 hour. When finished, the air in the system was purged with helium (He). The volatiles formed were then analyzed (Fig 2). The irradiated PC was analyzed by reactive pyrolysis with TMAH.

Result: Fig. 1 illustrates the expected degradation paths of PC. It is reported that the scission of the carbonate bond and the formation of a branched structure via rearrangement are the major degradation pathways. Therefore, BisA, should be the primary volatile degradation product and the degraded polymer should have branched structures. Fig. 2, shows the intensity of BisA peak increased by a factor of 10 when irradiated. This indicates that the scission of carbonate bonds in the polymer chain occurred repeatedly. Fig. 3 shows the Rx/PY results on the degraded polymer. With UV irradiation, peak A, a branched structure, was easily observed.

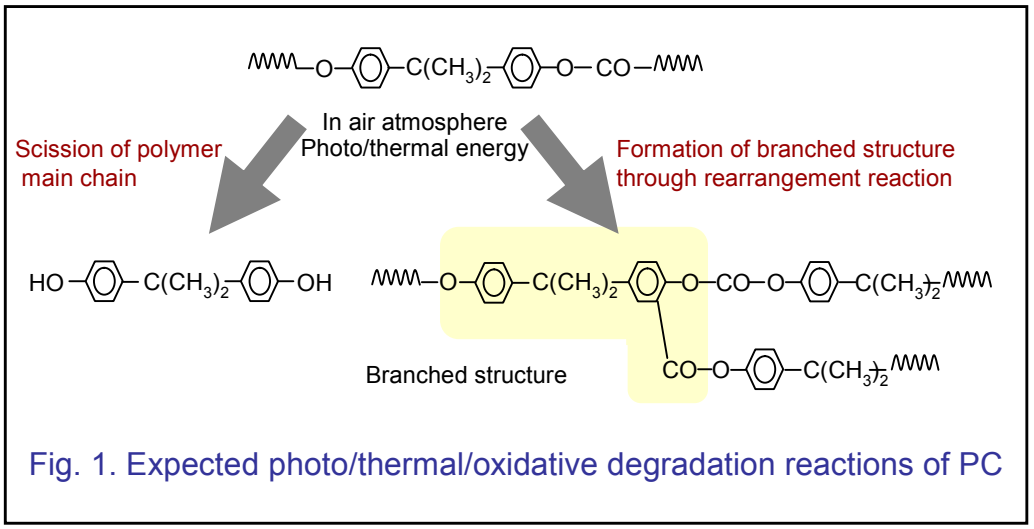

Fig. 1. Expected photo/thermal/oxidative degradation reactions of PC

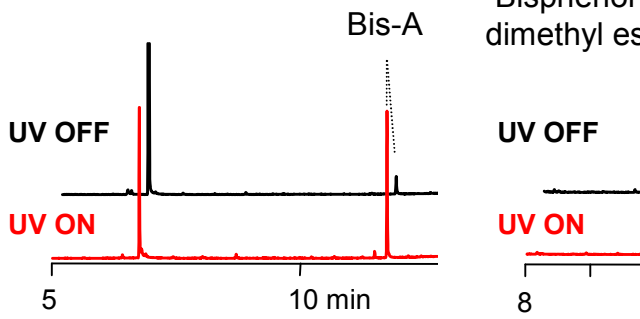

Fig. 2. Chromatograms of volatiles released from PC

Column: UA+-1(L 30 m, id. 0.25 mm, df 0.25 µm), Flow rate: 1 ml/min, Split ratio: 1/10, Sample: ca.15 µg (thin film), GC temp.: 40 - 300ºC (20ºC/min), Thermal desorption (TD) temp.: 100 - 350ºC (20ºC/min)

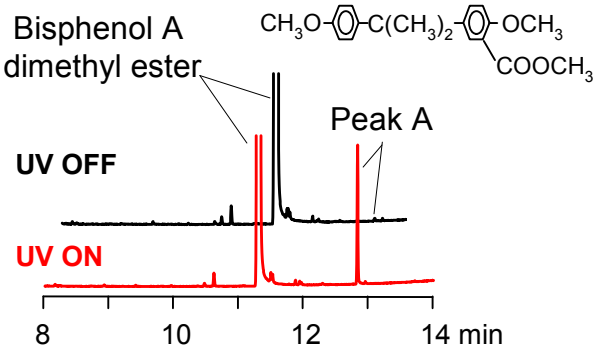

Fig. 3. Pyrograms obtained by reactive pyrolysis of the degraded PC

Py furnace temp.: 400ºC, Reagent: TMAH (25 wt. % in methanol, 3 µL), Split ratio: 1/50, other conditions identical to those in Fig. 2.

Ref: Multi-functional Pyrolyzer® Technical Note, PYA5-002E

L-3

Problem: Is there a way to analyze volatile degradation products from high impact polystyrene (HIPS) in photo/thermal/oxidative degradation tests?

Analysis: Volatiles released from HIPS when it is exposed to UV radiation can be analyzed using the micro UV irradiator with a xenon (Xe) lamp. 10 µL of a dichloromethane solution (2 mg/mL) of HIPS was placed in a sample cup. The HIPS sample was irradiated for one hour at 60ºC in air. Volatile degradation products were cryo-trapped at the head of the separation column. When the UV irradiation was finished, the air was purged with helium and the irradiated sample was thermally desorbed (60-250ºC). The GC/MS analysis of the trapped vapors was then conducted.

Result: Fig. 1 shows the chromatograms of the volatile degradation products from HIPS with and without UV irradiation. Benzaldehyde, acetophenone, and benzoic acid are the PS degradation products formed during the irradiation. 2-propenal is also observed. It is the volatile degradation product of butadiene present in HIPS.

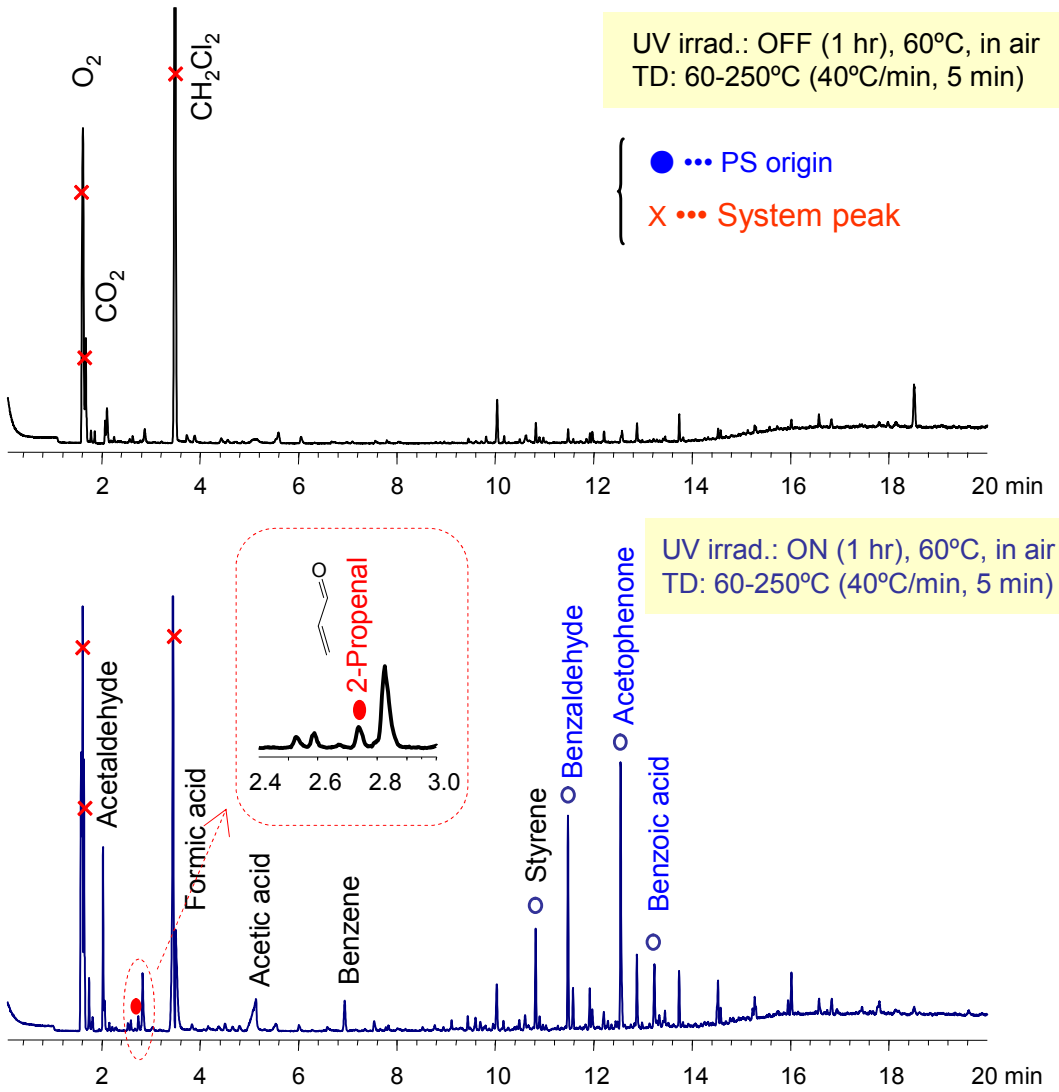

Fig. 1. Chromatograms of the volatile degradation products formed when HIPS is irradiated and not irradiated.

<UV irrad.> Micro UV irradiator: UV-1047Xe, irrad.: 1 hr, furnace temp.: 60ºC, atmosphere gas: 10 mL/min Air, split ratio:1/10
<GC/MS> Separation column: Ultra ALLOY+-1 (polydimethylsiloxane, L=30 m, i.d.=0.25 mm, df=0.5 µm), GC oven temp.: 40ºC(5 min)-240ºC (20ºC/min), GC injection temp.: 250ºC, carrier gas: 50 ml/min He, split ratio: 1/50

Ref: Multi-functional Pyrolyzer® Technical Note, PYA5-003E

L-4

Problem: Has UV-degraded high impact polystyrene (HIPS) been studied?

Analysis: UV-degraded HIPS was analyzed using evolved gas analysis (EGA)-MS. HIPS (2 mg/mL) was placed in a sample cup (two side openings) and irradiated for 30 min to 12 hours using the micro UV irradiator at a furnace temperature of 60ºC in air. EGA was performed.

Result: When a HIPS sample is irradiated for 1 hour using the micro UV irradiator, the peak apex decreases 10ºC, and the onset of pyrolysis decreases by 60ºC. Also, the peak becomes broader. Size-exclusion chromatography reveals that the average molecular weight decreases from 285,000 to 240,000, indicating that the polymer's main chain is degraded. A second HIPS sample was irradiated for 300 hours using a conventional Xe-weather meter. The peak apex decreases by 14ºC and the onset of pyrolysis decreases by 80ºC. The HIPS thermograms obtained after irradiation using the micro UV irradiator and the weather meter are almost identical. The micro UV irradiator provides comparable data to that obtained using a weather meter in much less time.

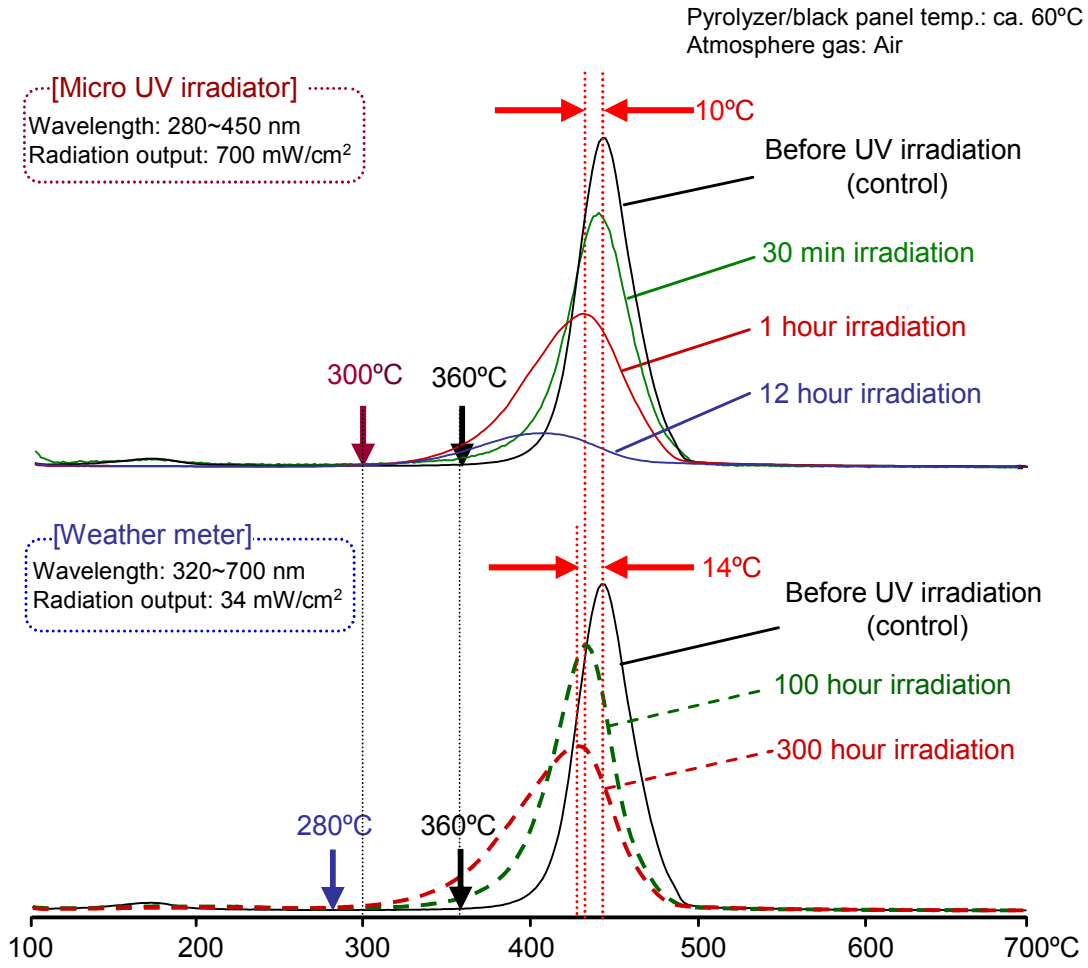

Fig. 1. Thermograms obtained before and after irradiation by UV/Py-GC/MS (top) and Xe weather meter (bottom).

Pyrolyzer temp.: 100 - 700ºC (20ºC/min), GC oven temp.: 300ºC, UADTM-2.5N (L=2.5 m、i.d. =0.15 mm), Carrier gas flow rate: 1 mL/min; He, split ratio: 1/50, sample:20µg

Ref: Multi-functional Pyrolyzer® Technical Note, PYA5-004E

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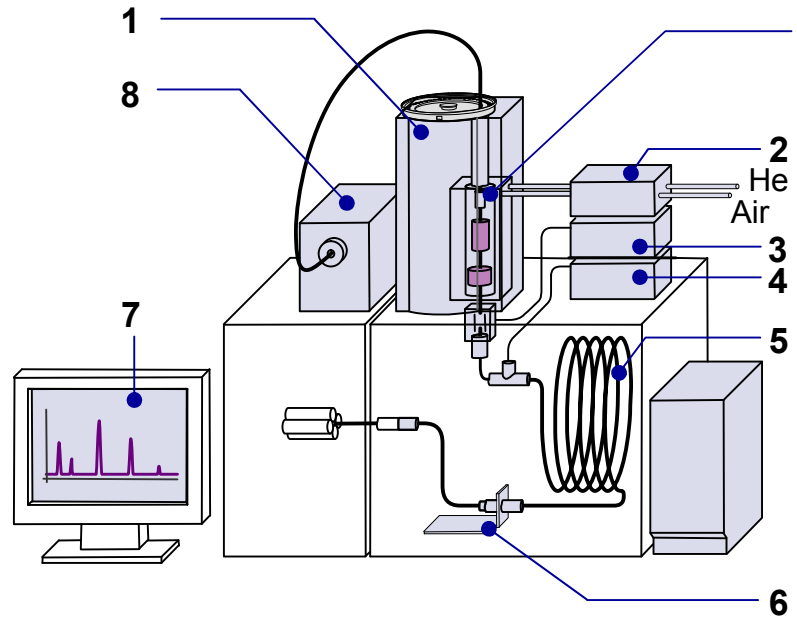
- **Polymer processing** : Polymer characterization techniques
- **Others** : Miscellaneous applications



Py-GC/MS system comprising Multi-Shot Pyrolyzer and supporting accessories

Multi-Shot Pyrolyzer (EGA/PY-3030D)

1. Auto-Shot Sampler (AS-1020E)
2. Carrier Gas Selector (CGS-1050Ex)
3. Selective Sampler (SS-1010E)
4. MicroJet Cryo-Trap (MJT-1030Ex)
5. Ultra ALLOY® metal capillary column
6. Vent-Free GC/MS adapter (MS402180)
7. F-Search system (search engine and libraries)
8. Micro UV irradiator (UV-1047Xe)

Multi-Shot Pyrolyzer EGA/PY-3030D

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