

# Solving Analytical Problems

Version 1.0

## using Multifunctional Pyrolyzer®

### Basic materials

- Polyethylene
- Polypropylene
- Polystyrene
- Polyurethane
- Nylon
- Epoxy
- Polycarbonate
- Rubber
- etc.

## Introduction to Frontier Laboratories

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

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

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

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



All information subject to change without notice.

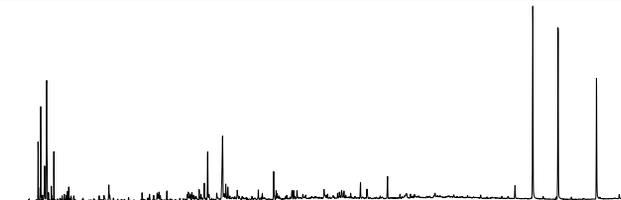
## Analytical problems and Frontier-Based Solutions

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**Problem:** How is the Double-Shot technique used to analyze acrylonitrile butadiene rubber (NBR)?

**Analysis:** Double-Shot technique is useful because volatile components are thermally desorbed at the first stage, then flash pyrolysis of the basic polymer follows. Analysis of NBR is described here as an example.

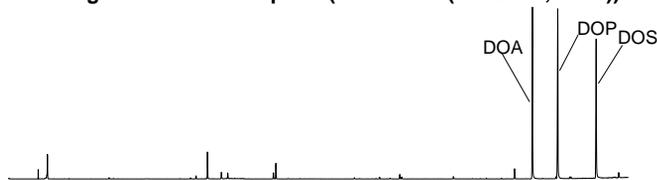
**Result:** Fig 1 shows a pyrogram of NBR by Single-Shot (flash pyrolysis) method. Products thermally decomposed and additives are shown on a single pyrogram, it is difficult to distinguish the peaks of basic polymer from those of additives. In the Double-Shot technique (Fig. 2); however, volatiles and additives are eluted off in the first step, whereas thermal decomposition products of basic polymer come off in the second step, allowing much easier identification of peaks. Conditions for thermal desorption and pyrolysis can be determined from EGA curve obtained in evolved gas analysis technique.



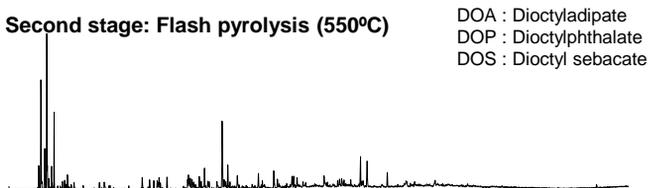
**Fig. 1 Pyrogram of NBR by Single-Shot Technique (TIC)**

PY: Double-Shot Pyrolyzer (PY-2020D), Detector : MS, Scan range :  $m/z=29-400$   
 Pyrolysis temp.: 550°C, Carrier gas : He, Column flow rate : 1.0 ml/min  
 Separation column : Ultra ALLOY-5 (5% phenyldimethylpolysiloxane), L=30 m, id=0.25 mm,  
 df=0.25  $\mu\text{m}$ , GC oven temp.: 40°C 3min ~ 10°C/min ~ 300°C (3 min), GC injection port  
 temp.: 320°C, Sample: 0.31 mg

**a. First stage: Thermal desorption (100~300°C (20°C/min, 5min))**



**b. Second stage: Flash pyrolysis (550°C)**



DOA : Diocyladipate  
 DOP : Diocylphthalate  
 DOS : Diocyl sebacate

**Fig. 2 Pyrogram of NBR by Double-Shot Technique**

See Fig. 1 above for analytical conditions

**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.

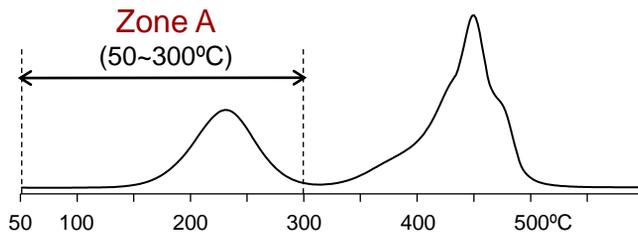


Fig.1 EGA thermogram of NBR

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 %

TD: 50~300°C

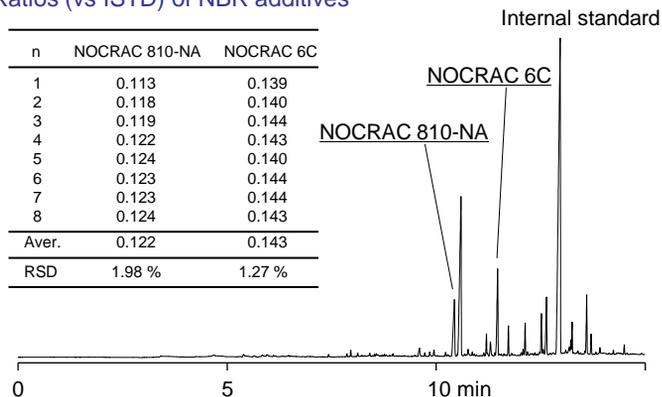


Fig. 2 Chromatogram for Zone A by (TD)-GC/MS analysis

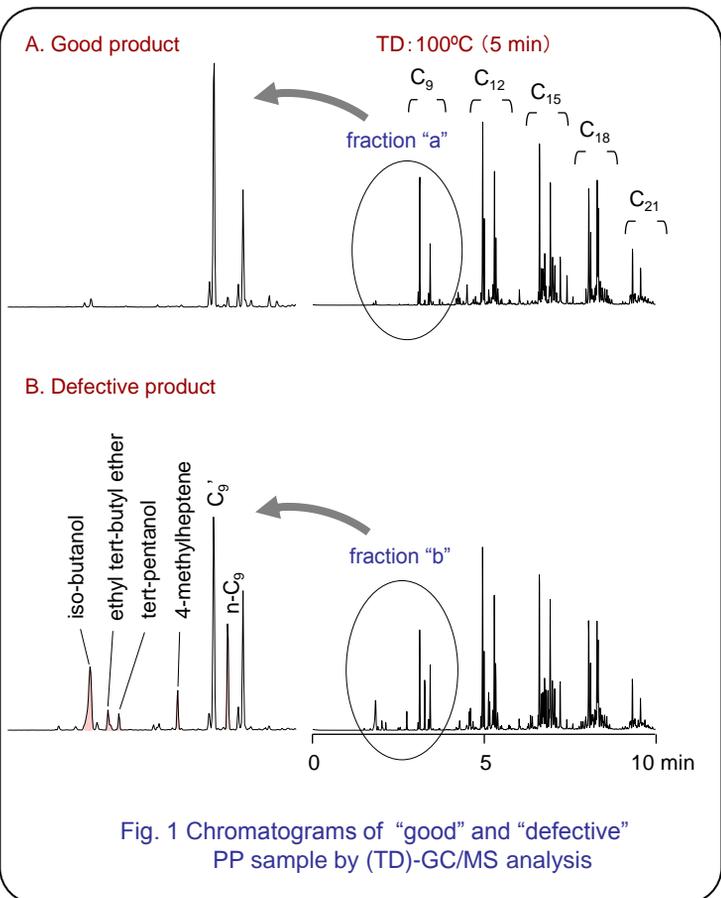
NOCRAC810-NA: N-Phenyl-N'-isopropyl-p-phenylenediamine  
 NOCRAC 6C: N-Phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine

3

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

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

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



**Problem:** High impact polystyrene (HIPS) is a polystyrene (PS) copolymerized with a few percents of butadiene rubber to increase impact resistance of PS. How can the rubber in HIPS be analyzed?

**Analysis:** Pyrolysis GC is used as a tool for quality control of HIPS. Here, quantitative analysis of a trace amount of butadiene present in HIPS using Double-Shot Pyrolyzer® is described.

**Result:** Fig. 1 shows a pyrogram of HIPS obtained at 550°C. Butadiene (B) and styrene (S), monomer components of HIPS, have been detected. Table 1 shows peak area ratios of B and S (B/S) in the pyrograms obtained repeatedly. The excellent reproducibility of RSD 0.62% was obtained. In the actual quantitative analysis, various mixing ratios of samples are used to produce a calibration curve.

Table 1 Peak Area Ratios of Butadiene (B) and Styrene (S) and Reproducibility

n	B/S(%)
1	1.249
2	1.244
3	1.246
4	1.254
5	1.233
Average	1.245
RSD (%)	0.62

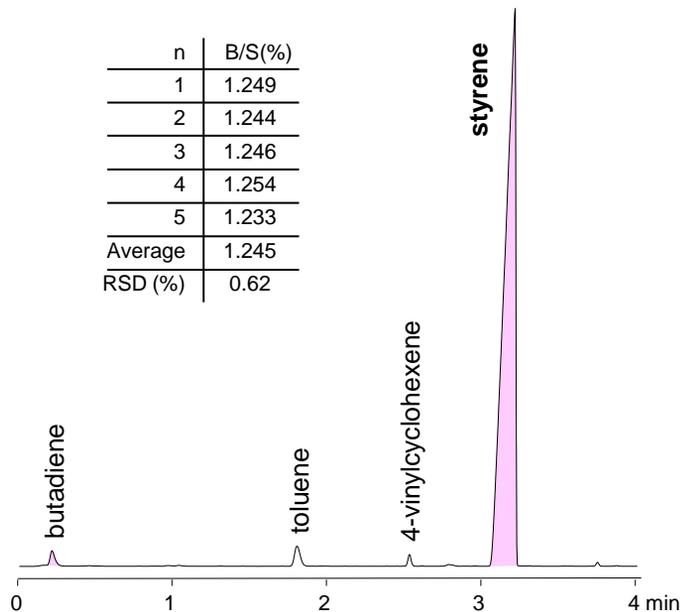


Fig. 1 Pyrogram of HIPS

Pyrolysis temp: 550°C, Separation column: Ultra ALLOY®-5 (5% diphenylpolysiloxane)  
Sample amount : 100µg, Detector : Hydrogen flame detector (FID)

**Problem:** How can the structural characterization of hydrogenated acrylonitrile-butadiene rubbers (NBRs) be done using Py-GC?

**Analysis:** Hydrogenated NBRs were prepared from NBR and Pd catalyst. Py-GC system had a vertical micro-furnace and was directly attached to a GC with an FID. About 70  $\mu\text{g}$  each of samples was pyrolyzed at 550°C. The identifications of peaks were done by a directly coupled GC-MS.

**Result:** Fig. 1 shows the pyrograms of NBR samples at 550°C before and after the hydrogenation that were obtained using a capillary column with poly(dimethylsiloxane) stationary phase. Characteristic peaks in the pyrogram of N-37(0) were butadiene (BD) monomer, BD dimer, and acrylonitrile (AN) monomer; whereas those of hydrogenated NBR consisted of a series of linear mononitriles (MN(A)s) up to C<sub>12</sub>, each of which consisted of a doublet corresponding to an  $\alpha$ -olefinic MN(A) (the former) and a saturated MN(A) (the latter). Another series of mononitrile positional isomers (MN(B)s) are also observed. HC peaks of each carbon number consisted of a triplet corresponding to an  $\alpha,\omega$ -diolefin,  $\alpha$ -olefin, and a n-alkane.

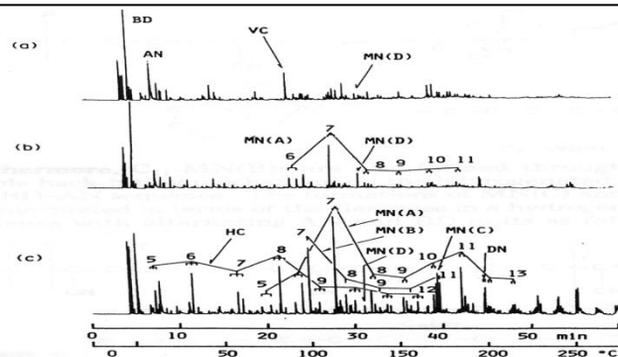


Fig. 1 Pyrograms of NBRs before and after hydrogenation at 550°C separated by a poly(dimethylsiloxane) column:

(a) N-37(0); (b) N-37(44); (c) N-37(98). See Table 1 for abbreviations.

Table 1 Characteristic Degradation Products from Hydrogenated NBR

Compound class	Abbreviation	Sequence
Butadiene	BD	B
Butadiene dimer (4vinylcyclohexane)	VC	BB
Acrylonitrile	AN	A
Hydrocarbons	HC	EE EEE
Mononitriles	MN(A)	EA EEEEA
	MN(B)	EA EEA
	MN(C)	EAE
	MN(D)	BA
	DN	AEA
Dinitriles	DN	AEA

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

**Problem:** Can the within-tree variations of lignin components in *Eucalyptus* be characterized by Py-GC?

**Analysis:** The wood block of *Eucalyptus* tree from western Australia was cryo-milled to a powder. Then the fine powder was pyrolyzed under He atmosphere and analyzed by GC/MS.

**Result:** Fig. 1 shows a typical pyrogram of a *Eucalyptus* sample obtained at 450°C and observed by FID. Pyrolyzates derived from lignin were observed as peaks 1 through 26. Table 1 shows the assignment of these peaks and also lists the relative molar yields among the 26 pyrolyzates from lignin for radial samples A-1 through A-7. The within-tree variation of the syringylpropane vs. guaiacylpropane (S/G) ratio in the radial direction obtained on the basis of the molar yields of the pyrolyzates showed the highest S/G ratio of 2.13 for sample A-1 at the extreme pith side. The S/G ratio then decreased gradually towards the bark with the lowest value of 1.57 for sample A-7. The within-tree axial variations were similarly determined.

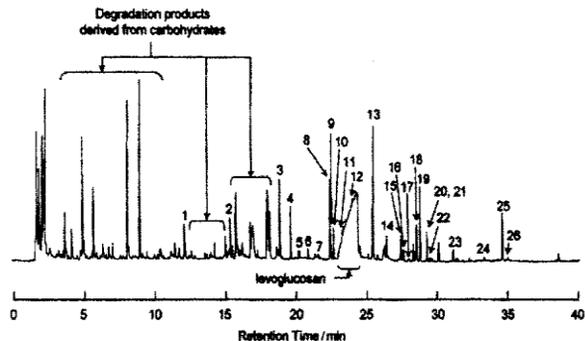


Fig. 1 Pyrogram of *Eucalyptus* obtained at 450°C  
(See below for peak assignments)

Table 1 Radial variation of pyrolyzates for samples at 3 m above ground  
(S: syringyl unit, G: guaiacyl unit)

Peak No.	Compound	Origin	Molar yield (%)						
			A-1	A-2	A-3	A-4	A-5	A-6	A-7
1	Guaiacol	G	4.90	4.96	4.96	4.41	4.42	4.12	5.38
2	4-Methylguaiacol	G	5.55	4.95	4.55	4.64	5.04	5.01	4.47
3	Vinylguaiacol	G	6.93	6.75	6.28	6.18	6.42	7.01	5.93
4	Syringol	S	9.24	8.49	9.45	8.17	9.94	7.55	8.06
5	Eugenol	G	0.94	0.85	0.76	0.63	0.94	1.07	1.32
6	Vanillin	G	1.49	1.36	1.49	1.60	1.79	1.88	2.21
7	cis-Isoeugenol	G	0.45	0.43	0.44	0.46	0.57	0.50	0.38
8	Methylsyringol	S	9.29	8.75	8.18	7.78	8.60	8.03	6.54
9	Homovanillin	G	1.86	1.63	1.41	1.63	1.40	1.77	1.44
10	trans-Isoeugenol	G	3.80	3.48	3.32	3.35	4.17	4.03	3.16
11	Acetoguaiacene	G	1.00	0.93	1.00	1.00	0.95	0.94	1.01
12	Guaiacylacetone	G	0.61	0.48	0.58	0.21	0.61	0.65	0.40
13	Vinylsyringol	S	14.01	14.37	12.68	13.72	11.29	11.80	11.99
14	Allylsyringol	S	2.37	2.43	1.98	1.77	2.04	2.04	1.58
15	Syringaldehyde	S	5.16	5.23	5.22	5.48	6.04	6.32	6.51
16	cis-Propenylsyringol	S	1.46	1.29	1.22	1.18	1.43	1.35	1.06
17	cis-Coniferyl alcohol	G	0.32	0.53	0.64	0.66	0.64	0.60	0.71
18	Homosyringaldehyde	S	3.71	2.92	2.79	2.82	2.71	2.85	1.92
19	trans-Propenylsyringol	S	9.70	8.40	7.91	7.42	8.22	8.19	6.61
20	trans-Coniferylaldehyde	G	1.25	1.41	1.49	1.54	1.63	1.35	1.79
21	Acetosyringone	S	2.75	3.11	3.29	3.39	3.59	3.42	5.94
22	trans-Coniferyl alcohol	G	2.46	5.17	6.88	7.69	6.18	6.42	9.25
23	Syringylacetone	S	1.75	1.66	1.59	1.54	1.43	1.45	1.26
24	cis-Sinapyl alcohol	S	0.72	1.27	1.57	1.53	1.24	1.19	1.77
25	trans-Sinapaldehyde	S	6.67	6.71	6.63	6.62	6.69	7.39	7.69
26	trans-Sinapyl alcohol	S	1.61	2.44	3.69	4.58	2.02	2.87	3.62
Total			100	100	100	100	100	100	100

**Problem:** The lignin in hardwoods consists of syringyl propane units (S) and guaiacyl propane units (G). The S/G ratio varies depending on origins and growth conditions of the trees. What analytical techniques are available to measure them?

**Analysis:** Eleven wood samples taken from *Eucalyptus* trees grown under the same condition and the seeds collected from four different habitats in Australia were cryo-milled into fine powders, and were pyrolyzed at 450°C under He using a Py-GC system. The distribution of lignin-derived pyrolyzates was processed using PCA software.

**Result:** Fig. 1 shows a pyrogram of a sample grown from seeds collected from Murchison River. Pyrolyzates derived from lignin were observed as peaks S-1 through S-13 and G-1 through G-13. The PCA method was applied in which information from multivariate data was converted into individual variables. Fig. 2 shows a score plot of the first and second principal components for samples grown from 4 different origins, showing rough grouping of the samples according to the origin of the seeds.

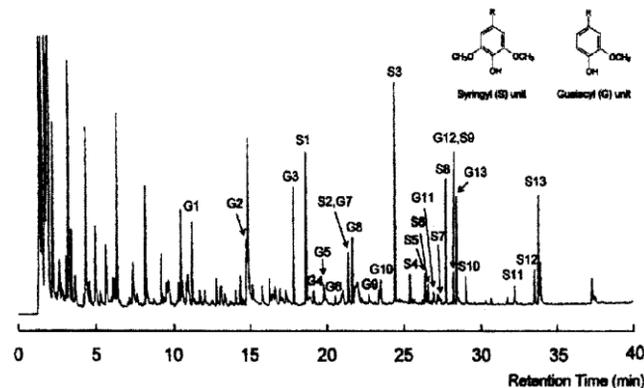


Fig. 1 Pyrogram of *Eucalyptus* (M-1) obtained at 450°C observed by FID

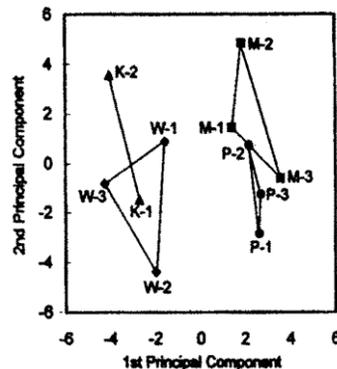


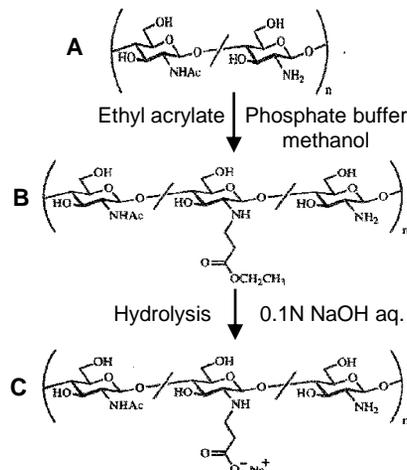
Fig. 2 Score plot of the first and second principal components for the trees.

P, Petford; M, Murchison River; W, Wrotham Park; K, Katherine River

**Problem:** Chitin, abundant in nature, is an important amino polysaccharide. Is there a way to analyze chitin?

**Analysis:** Here, Michael-type nucleophilic addition of partially deacetylated chitin to ethyl acrylate was evaluated by Py-GC.

**Result:** The polymer reaction of **A** with ethyl acrylate to the D-glucosamine residue was carried out at 40°C (Scheme 1). Hydrolysis of pendant ester groups of the product was observed in phosphate buffer solution, while **B** 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 **A**. Degrees of substitution (DS) to the amino group of the D-glucosamine residue of **B** were determined by <sup>1</sup>H NMR spectroscopy using the methyl protons of the N-acetyl-D-glucosamine residue of **B** and the newly formed methylene protons adjacent to the 2-amino group of the D-glucosamine residue. DS values determined based on -NHCH<sub>2</sub>- were further supported by quantitative analysis of Py-GC technique.



Scheme 1

Synthesis of N-selective ester functionalized chitin derivative and water-soluble carboxy ethylchitin.

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

Run No.	1		Yield in mg (%)	Product polymer		
	in mg	-NH <sub>2</sub> of <b>A</b> in mmol		Degree of substitution (DS)		
				<sup>1</sup> H NMR Based on -CO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	<sup>1</sup> H NMR Based on -NHCH <sub>2</sub> -	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, 40°C; time. 240 hr

**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 550°C.

**Result:** Fig.1 shows the pyrogram for the blended 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.

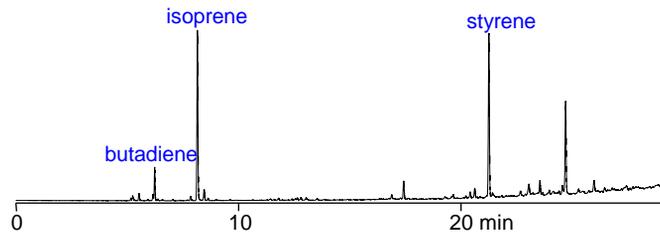


Fig.1 Pyrogram of a blended rubber

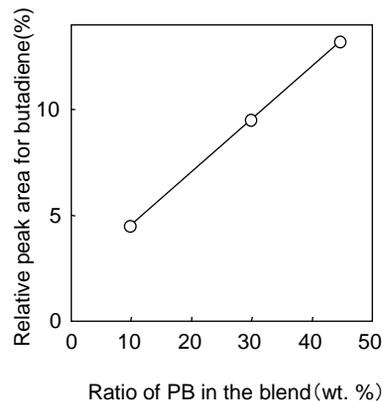


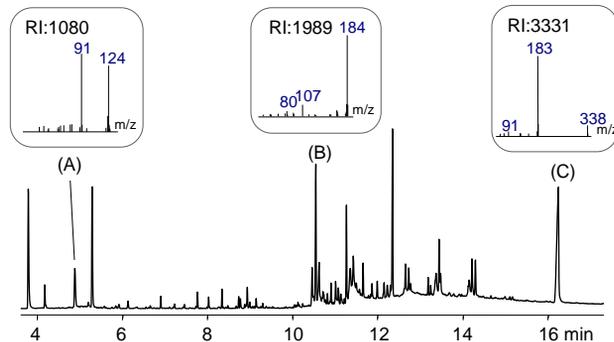
Fig.2 Calibration curve for PB in the blend

**Problem:** Is there a library search program that allows for the identification of unknown antidegradants used in rubbers?

**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

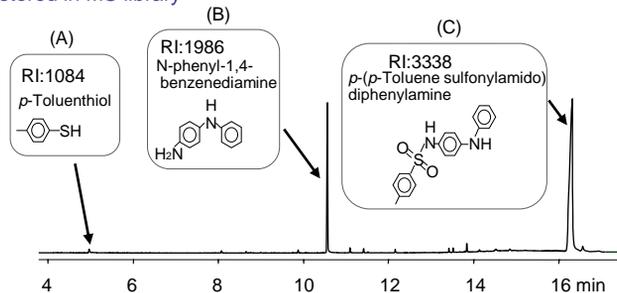


Fig. 1 Chromatogram obtained by (TD)-GC/MS technique

**Problem:** Is there a simple way to determine the terminal groups of polycarbonate (PC)?

**Analysis:** Microgram quantities of the PC sample are placed in the sample cup along with 3  $\mu\text{L}$  of a 25 wt% of methanol solution of tetramethyl ammonium hydroxide (TMAH). The sample is then analyzed using a reactive pyrolysis GC (FID) method

**Result:** Fig.1 shows the pyrogram of the reactive pyrolysis of the PC sample synthesized by solvent method. Basic TMAH selectively cleaves the ester bond, and the resulting products undergo immediate etherification. The pyrogram clearly shows that the methyl ether of bisphenol A is the main component. The presence of bisphenol A and the methyl ether of *t*-butylphenol demonstrates that the PC has terminal groups of *t*-butylphenol. Additionally, it is possible to estimate the average molecular weight from the relative peak intensity of the product derived from the terminal groups against that from the main chain.

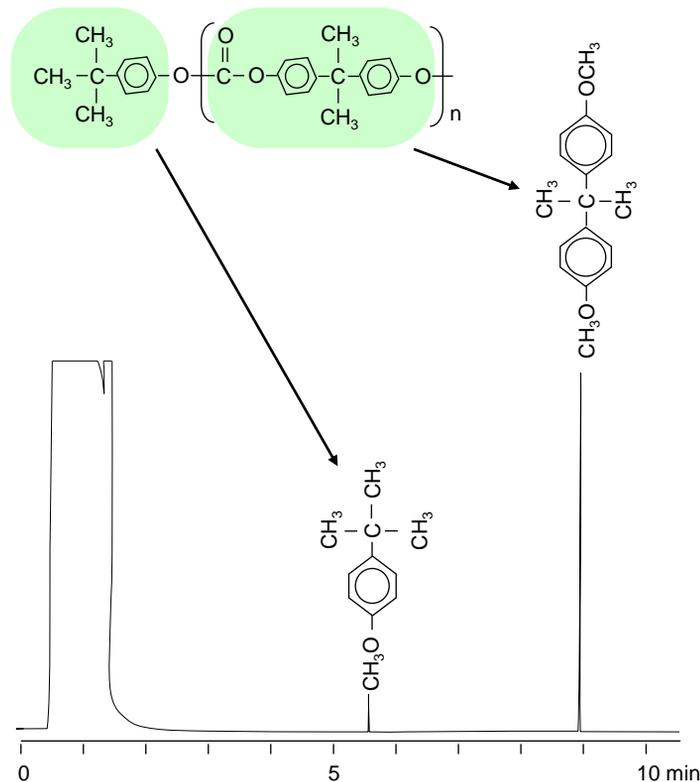


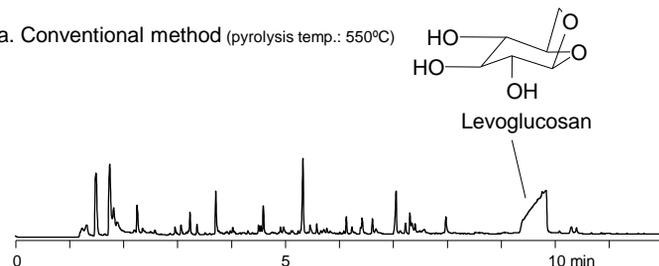
Fig.1 Reactive pyrogram of PC with TMAH reagent (Pyrolyzed at 400°C)

**Problem:** Levoglucosan is contained in cellulose pyrolyzates and is used as an index, but its reproducibility in quantitative analysis is poor. Is there a better way?

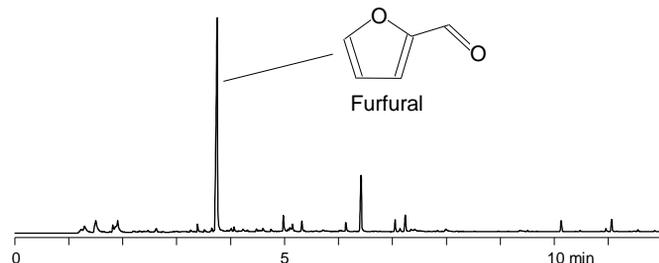
**Analysis:** 5  $\mu\text{L}$  of aqueous solution of cobalt sulfate (140 g/L) is added to 0.2 g of a cellulose sample, then allows it to dry. The dried sample is then subjected to reactive pyrolysis.

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

a. Conventional method (pyrolysis temp.: 550°C)



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



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

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

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

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

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

**Result:** 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.

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

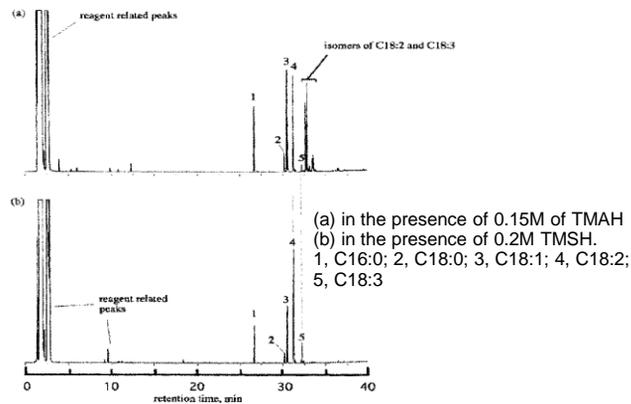


Table 1 Chemical composition and recovery of fatty acid components in soybean oil obtained by one-step THM-GC

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

\*Offline transmethylation by TMSH followed by GC measurement

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

**Problem:** How does inorganic salts (existing as impurities) influence the reactive Py-GC analysis in the presence of organic alkali?

**Analysis:** Entirely aromatic polyester was used as a polymer sample. After the sample was cold-ground, either tetramethylammonium hydroxide (TMAH) or TMAH solution containing KOH was added to the sample. Then it was subjected to reactive Py-GC for analysis.

**Result:** Fig. 1(a) shows pyrograms of the polyester obtained by reactive Py-GC in the presence of either (a) TMAH or (b) TMAH-KOH. While the DMB peak intensity stayed almost the same regardless of the presence of KOH, the peak intensities for MMB and DMT significantly decreased or no peak observed when using TMAH containing KOH. Further, similar experiments using TMAH containing KCl or NaCl showed diminished peak intensities, though not so dramatic as with KOH. It was shown that methylation of compounds containing carboxyl groups is significantly inhibited by the presence of inorganic salts.

An aromatic polyester sample, prepared with *p*-hydroxybenzoic acid (PHB), terephthalic acid (TA) and 4,4'-biphenol (BP) (PHB:TA:BP = 2:1:1)

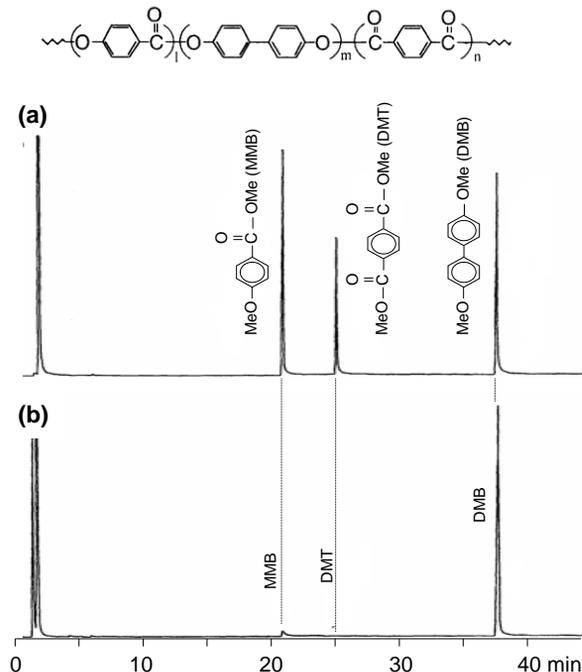


Fig. 1 Comparison of pyrograms obtained by reactive pyrolysis in the presence of (a) TMAH and (b) TMAH and KOH

**Problem:** How can the average molecular weight of polycarbonate be determined using reactive Py-GC in the presence of organic alkali?

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

**Result:** Fig. 1 shows a pyrogram of the PC sample obtained at 400°C in the presence of TMAH. *p*-*tert*-butylanisole (peak A) and the dimethylether of bisphenol-A (peak B), derived from the end groups and the PC main chain, respectively, are observed. Because both terminals in the SM-PC molecules are completely end-capped with *p*-*tert*-butylphenoxy groups, the average molecular weight ( $M_n$ ) can be estimated from the two peak intensities (formulae on the right bottom): 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 empirically determined effective carbon numbers (ECN) of the respective compounds for a flame ionization detector. The values of 254 and 326 in equation 2 are the MWs of the monomer unit and the two end groups, respectively.

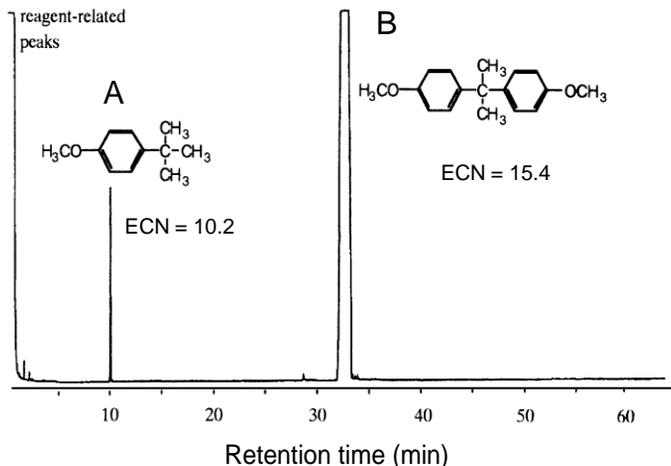


Fig. 1 Pyrograms of a PC sample obtained at 400°C in the presence of TMAH.

Furnace temp.: 400°C, GC oven temp.: 50°C - 300°C (4°C/min)  
 Separation column: poly(dimethylsiloxane), L=25 m, id=0.25 mm, df=0.25 µm  
 Column flow rate: 1.3 ml/min, Detector: FID

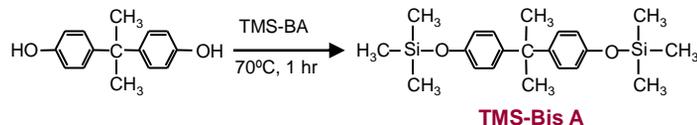
$$DP = \frac{I_B / 15.4}{(I_A / 10.2) / 2} \quad (1)$$

$$\overline{M}_n = DP \times 254 + 326 \quad (2)$$

**Problem:** How can the residual bisphenol A (Bis A) in polycarbonate (PC) be determined using a Double-Shot Pyrolyzer?

**Analysis:** N,O-bis(trimethylsilyl)acetamide (TMS-BA) is added to dichloromethane solution of PC, and then is heated to effect the reaction. The reaction mixture is measured by thermal desorption (TD)-GC/MS method at 300°C.

**Result:** TMS derivatization of Bis A is shown in Scheme 1, and the chromatogram obtained by thermal desorption is shown in Fig. 1. Both of the terminal hydroxyl groups of Bis A are TMS-derivatized to give 2,2-bis(4'-trimethylsilyloxyphenyl)propane (TM-Bis A), and its polarity becomes decreased. Therefore, absorption at active points in separation column is greatly suppressed. The reproducibility in quantitative analysis was found to be 4.7% RSD at Bis A concentrations around 1000ppm.



Scheme 1 TMS derivatization reaction with Bis A

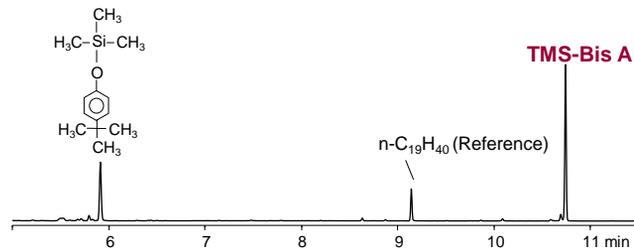


Fig. 1 Chromatogram of a TMS-derivatized PC sample obtained by (TD)-GC/MS

Separation column : Ultra ALLOY<sup>+</sup>-5 30M-0.25F  
GC oven temperature : 100°C~20°C/min~300°C(5min)

**Problem:** Are there any examples of qualitative analysis of fatty acids in algae using reactive Py-GC/MS with no pretreatment?

**Analysis:** 0.2 mg of dried algae was placed in a sample cup, 10  $\mu\text{L}$  of trimethylsulfonium hydroxide (TMSH) in methanol (0.2M) was added and the cup was dropped into the pyrolyzer's furnace (350°C) under He atmosphere. The gas-phase reactions occurred instantaneously. The methylated acids were separated and analyzed using GC/MS.

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

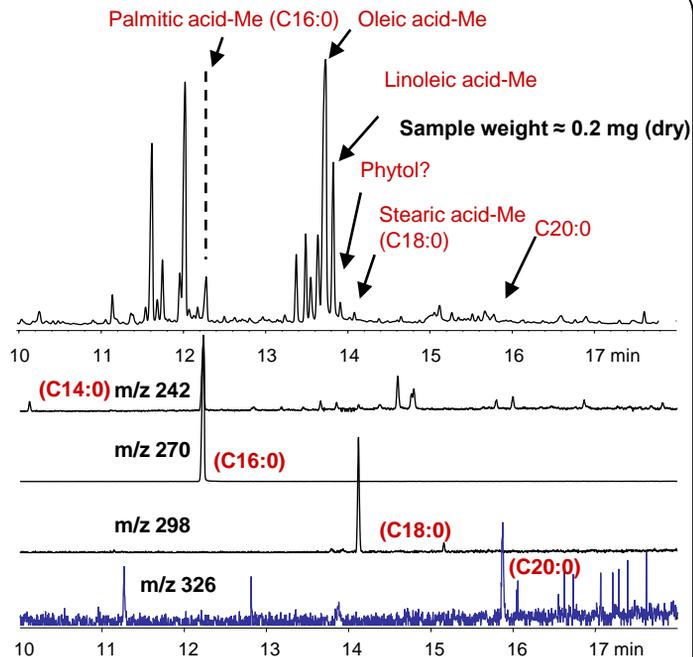


Fig. 1 Pyrogram of dried algae obtained by reactive Py-GC/MS

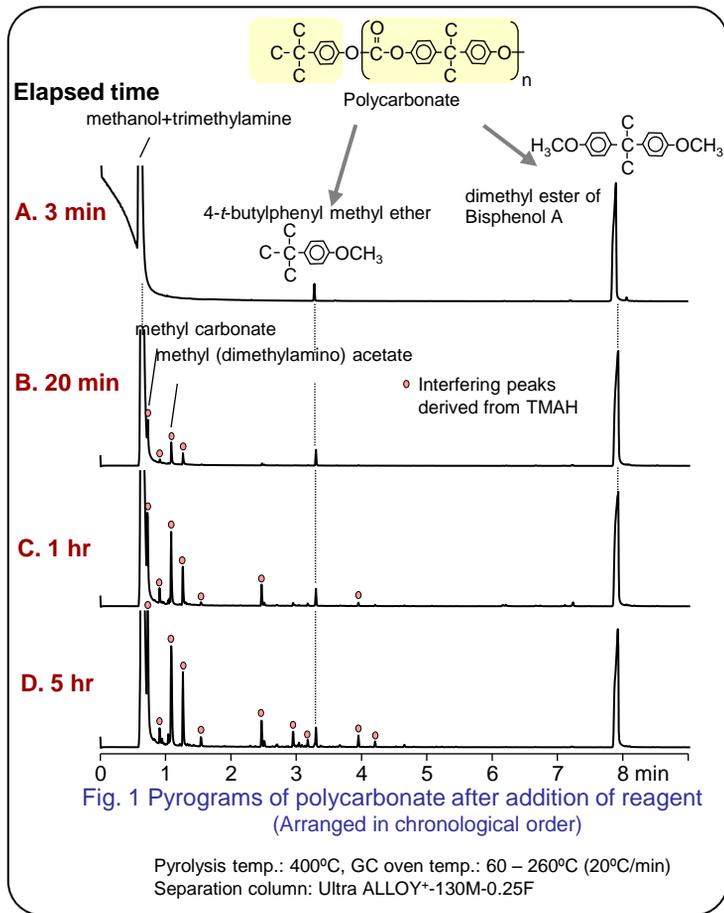
<Reactive pyrolysis conditions>

Pyrolysis temp.: 350°C, separation column: UA-5 (MS/HT) 30m, 0.25mm i.d., DF=0.25 $\mu\text{m}$ , 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  $\mu\text{L}$

**Problem:** Reactive Py-GC in the presence of a strong alkali such as tetramethyl ammonium hydroxide (TMAH), is used for the precise characterization of condensation polymers and fatty acids. Is there any effect that should be noted regarding the time interval between adding the reagent and the actual analysis?

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

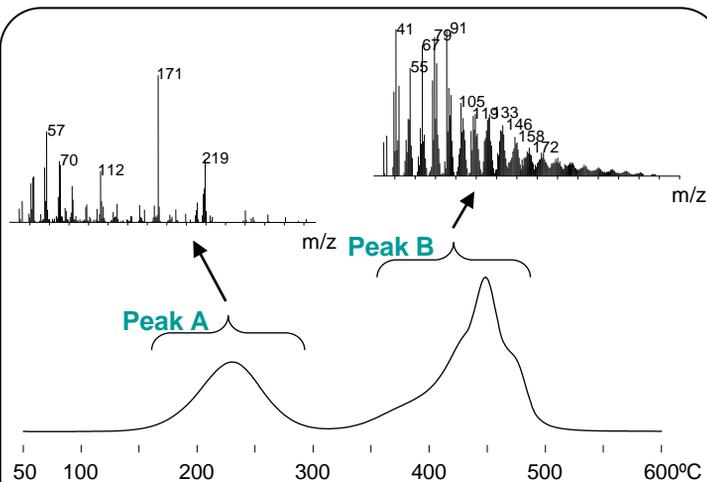
**Result:** Fig. 1 shows pyrograms obtained at different time intervals after the addition of TMAH. Pyrogram A had a peak for the dimethyl ester of bisphenol A and the methyl ester of 4-*t*-butylphenol, which originates from the terminal group. As the time interval increases, the peak intensities and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



**Problem:** Have rubber components been analyzed using EGA-MS technique?

**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.:50–600°C (10°C/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. : 300°C  
 Sample : ca. 0.5 mg, MS scan range: m/z=29-400, Scan speed: 0.1 scans/sec  
 PY-GC interface temp.: 320°C (AUTO mode)

**Table 1** Result of Library Search on Peak B

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

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