

# Solving Analytical Problems

using Multi-functional Pyrolyzer<sup>®</sup>

Version 1.0

## Processed materials

- Textiles
- Fibers
- Films
- Paper
- 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.

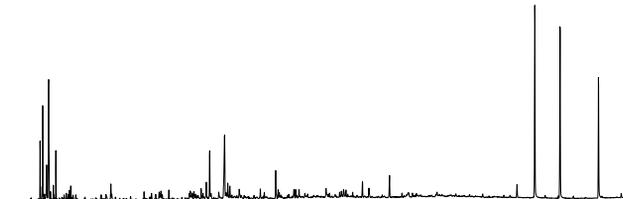
## Analytical problems and Frontier-Based Solutions

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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.

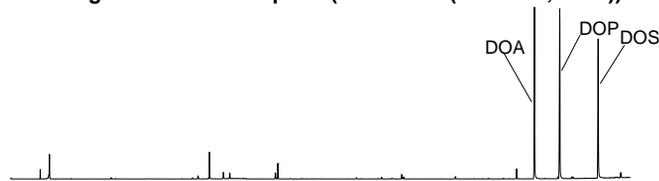
**Result:** Fig 1 shows a pyrogram of NBR by Single-Shot (flash pyrolysis) method. Products thermally decomposed and additives are shown on a single pyrogram, it is difficult to distinguish the peaks of basic polymer from those of additives. In the Double-Shot technique (Fig. 2); however, volatiles and 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.



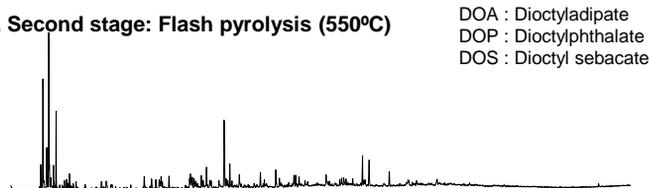
**Fig. 1 Pyrogram of NBR by Single-Shot Technique (TIC)**

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)**



**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.

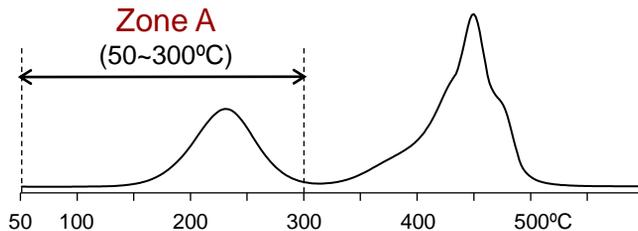


Fig.1 EGA thermogram of NBR

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 %

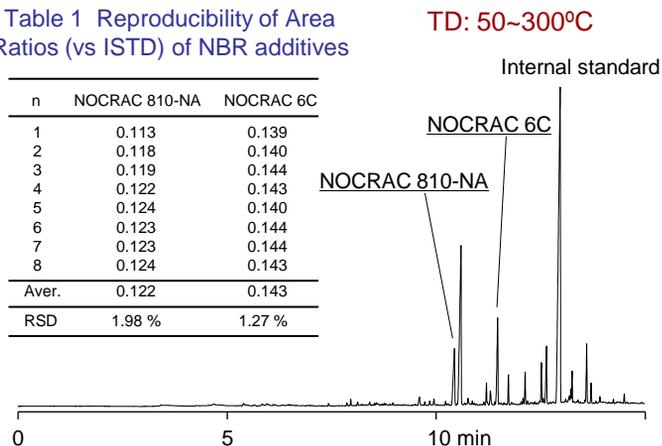


Fig. 2 Chromatogram for Zone A by (TD)-GC/MS analysis

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



**Problem:** Is there an example in which a ceramic composite material was analyzed by the Double-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 (Wiley 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

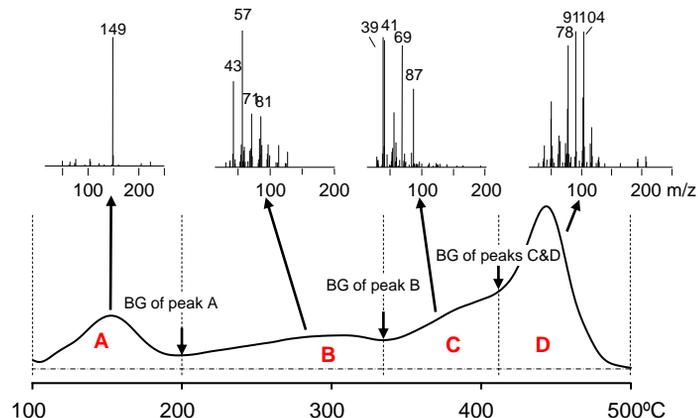


Fig. 1 EGA Curve of Ceramic Composite Material (Injection molding)

Pyrolyzer 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)

**Problem:** How can polysiloxanes be quantitatively determined?

**Analysis:** Samples are pyrolyzed under nitrogen atmosphere. Pyrolyzates are separated and analyzed by Py-GC/MS.

**Result:** Fig. 1 shows typical pyrograms of dimethyl/methylphenyl substituted polysiloxanes. Table 1 lists component ratios of various siloxane copolymers obtained from pyrograms together with reference components. It is found that expected components are in a good agreement with nominal ones. This result demonstrates that component analysis of siloxane copolymers can be accomplished with a high precision by use of Py-GC/MS technique.

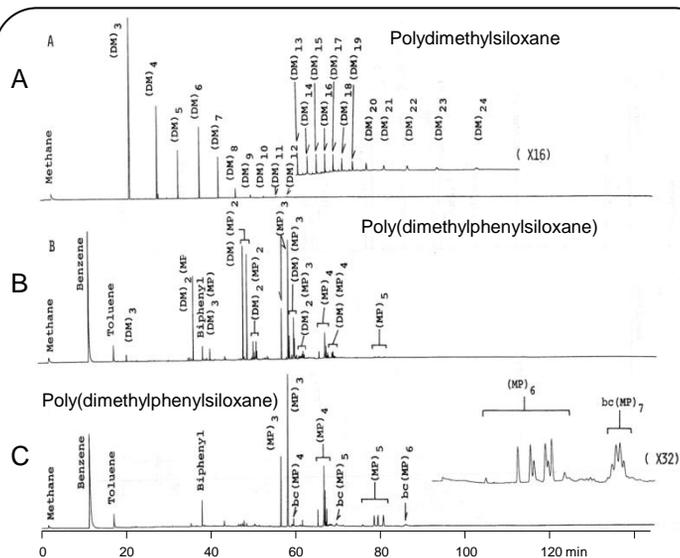


Fig. 1 Pyrograms of dimethyl/methylphenyl substituted polysiloxane

Table 1 Nominal and expected components of siloxane copolymers

Sample	Nominal component mol%	Expected component mol%
OV-3	DM:MP = 80:20	DM:MP = 82.5:17.5
OV-7	DM:MP = 60:40	DM:MP = 61.8:38.2
OV-11	DM:MP = 30:70	DM:MP = 31.1:68.9
OV-25	MP:DP = 50:50	MP:DP = 46.5:52.5
SE-52	DM:DP = 95: 5	DM:DP = 94.9: 5.1
XE-60	DM:MC = 50:50	DM:MC = 45.3:54.7

DM: dimethylsiloxane, MP: methylphenylsiloxane  
DP: diphenylsiloxane, MC: 2-cyanoethylmethylsiloxane

**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

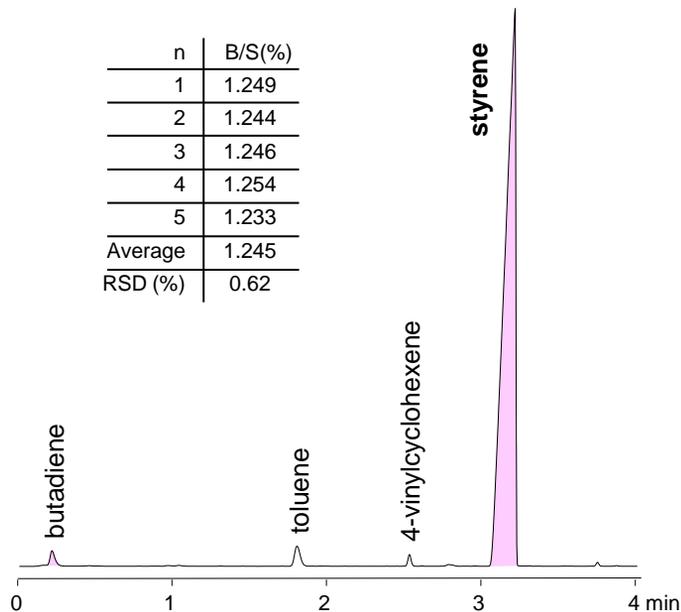


Fig. 1 Pyrogram of HIPS

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

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

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

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

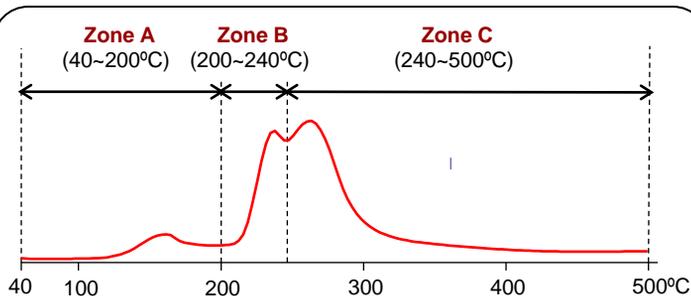


Fig.1 Thermogram of food wrap film

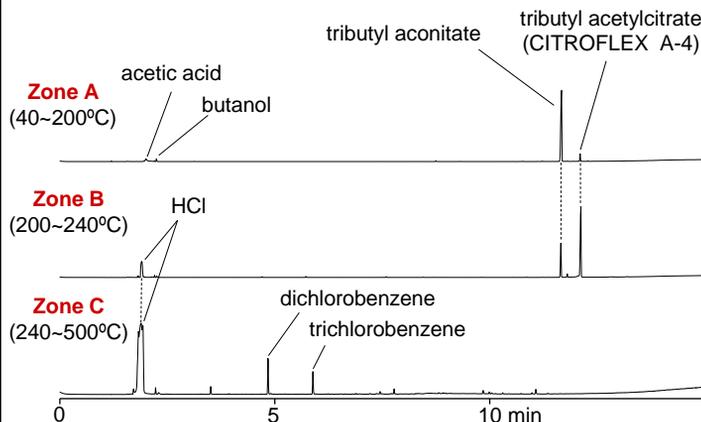


Fig. 2 Chromatograms for Zones A through C by Heart-Cut EGA-GC/MS method

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

**Analysis:** The analysis can be performed using a Double-Shot Pyrolyzer. Using EGA-MS technique, EGA profile is obtained by programmed pyrolysis from 40 to 600°C at a ramp rate of 30°C/min. Then, Zone A and Zone B of the EGA profile are analyzed by (TD)-GC/MS using MicroJet Cryo-Trap (MJT-1030E)

**Result:** Fig. 1 shows the EGA profile acquired using EGA-MS technique. The results of (TD)-GC/MS analysis of Zones A and B obtained utilizing MicroJet Cryo-Trap are shown in Fig. 2. In Zone A, volatile acetic acid, and fatty acids and their derivatives as plasticizer were found. In Zone B, olefinic hydrocarbons of C<sub>6</sub>, C<sub>9</sub>, C<sub>12</sub>, and C<sub>15</sub> derived from pyrolysis of polypropylene, and ε-caprolactam, monomer of nylon-6, were observed.

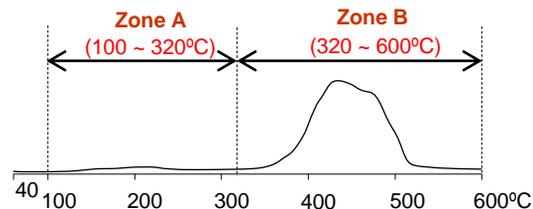


Fig. 1 EGA Profile of Polypropylene + Nylon

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

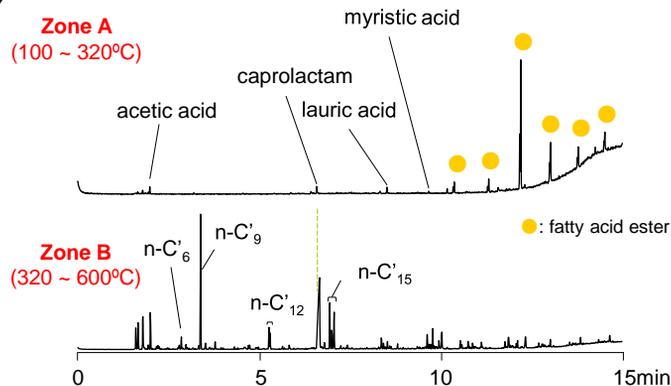


Fig. 2 Analysis Results of Zones A and B of Polypropylene + Nylon

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

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

**Analysis:** Using Double-Shot Pyrolyzer®, evolved gases from various food wrap films that were exposed to 100°C 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

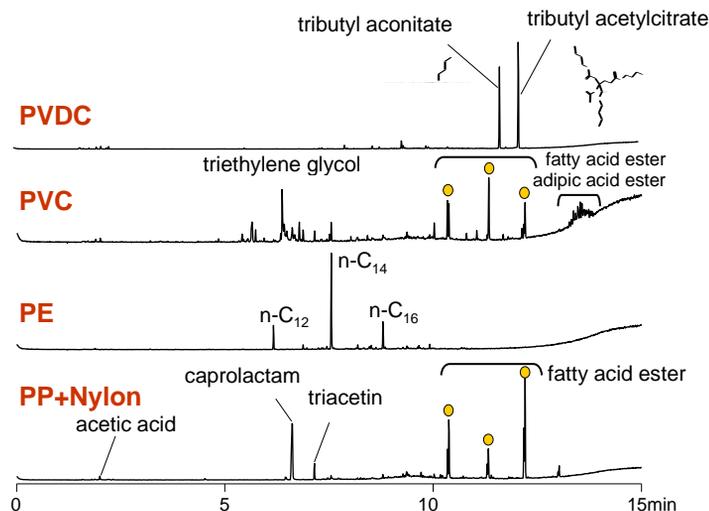


Fig. 1 Chromatograms of evolved gases from food wrap films exposed to 100°C for 10min

Thermal desorption temp: 100°C, Carrier gas: He, Cryo trap: 10 min, separation column: Ultra ALLOY-5, GC oven temp: 40°C–320°C (20°C/min), MS scan range: m/z=29–400

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

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

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

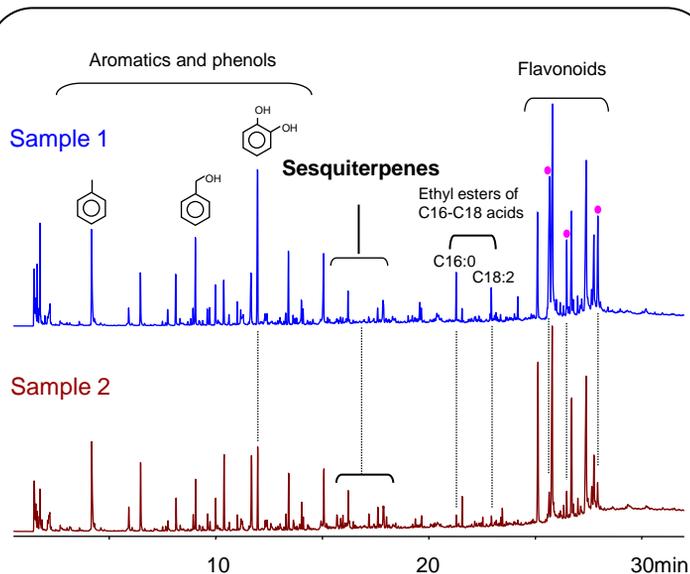


Fig. 1 TIC pyrograms of two different propolis samples

Double-Shot Pyrolyzer: PY-2020ID

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

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

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

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

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

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

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

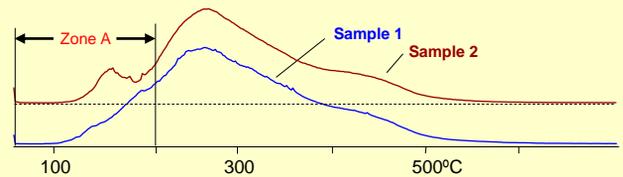


Fig. 1 EGA thermograms of different propolis

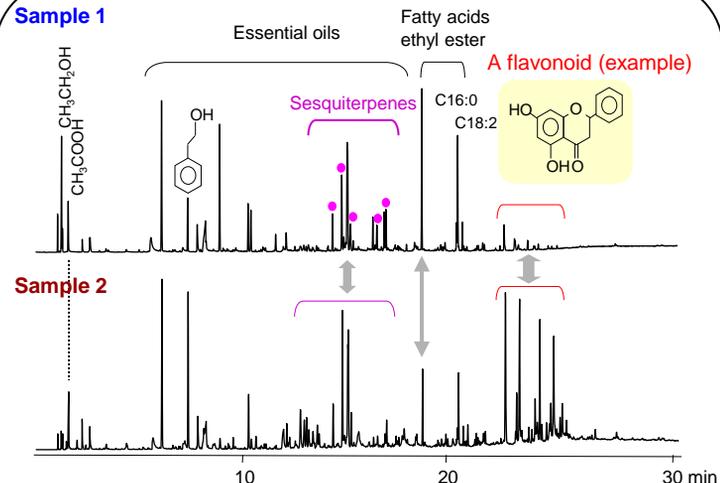


Fig. 2 Chromatograms of 2 types of propolis obtained from Zone A

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

GC oven temperature : 40°C~10°C/min~300°C (5min)

**Problem:** How can 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.

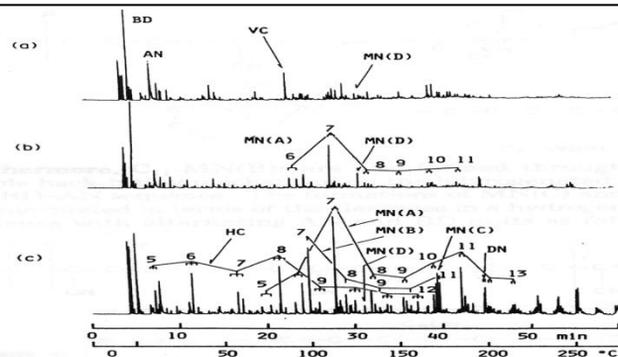


Fig. 1 Pyrograms of NBRs before and after hydrogenation at 550°C separated by a poly(dimethylsiloxane) column: (a) N-37(0); (b) N-37(44); (c) N-37(98). See Table 1 for abbreviations.

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

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

Table 1 Characteristic Degradation Products from Hydrogenated NBR

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

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

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

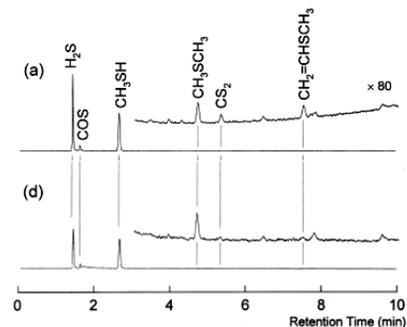


Fig. 1 Pyrograms of photo degraded silk samples at 600°C observed by SCD: (a) not exposed and (b) exposed for 52 days

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

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

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

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

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

**Problem:** 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.

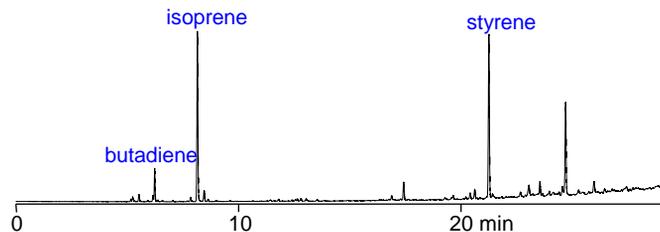


Fig.1 Pyrogram of a blended rubber

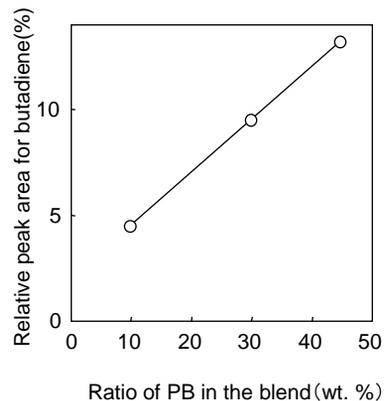


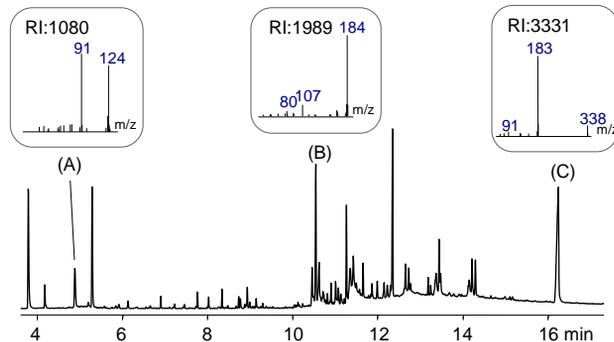
Fig.2 Calibration curve for PB in the blend

**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

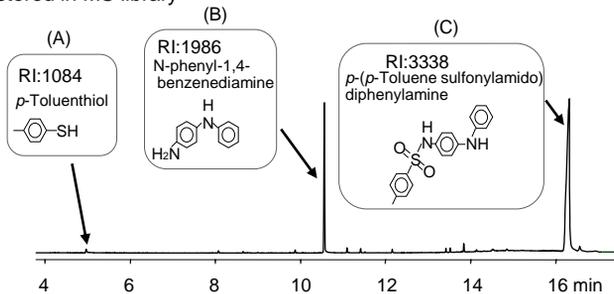


Fig. 1 Chromatogram obtained by (TD)-GC/MS technique

**Problem:** How can co-monomers of polybutylene terephthalate (PBT) be analyzed by Py-GC technique using the Double-Shot Pyrolyzer?

**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 monomers 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 monomers of dimethyl derivatives of terephthalic acid and mono and dimethyl derivatives of 1,4-butanediol.

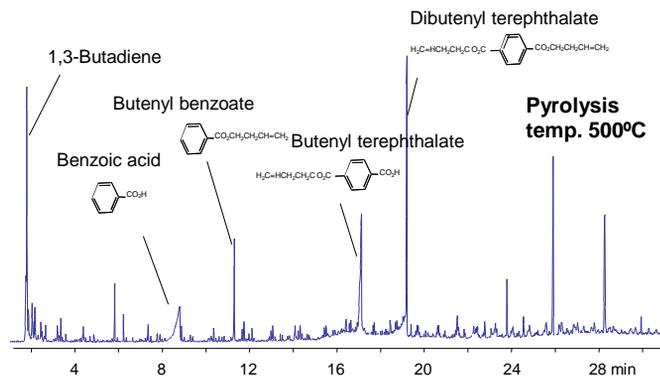


Fig. 1 Pyrogram Obtained by Flash Pyrolysis of PBT

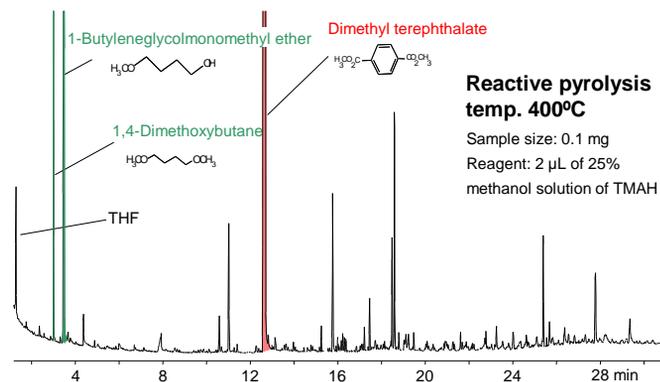


Fig. 2 Pyrogram Obtained by Reactive Pyrolysis of PBT

Carrier gas: He, Injection port pressure: 103kPa, Split ratio: 1/60  
Separation column: Ultra ALLOY<sup>+</sup>-5 (5% diphenyl 95% dimethylpolysiloxane), L=30 m, Id=0.25 mm, df=0.25 µm, GC oven temp: 38°C–300°C (20°C/min)

**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  $\mu\text{g}$  of a cryomilled PC sample was subjected to reactive Py-GC at 400°C in the presence of 1  $\mu\text{L}$  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.

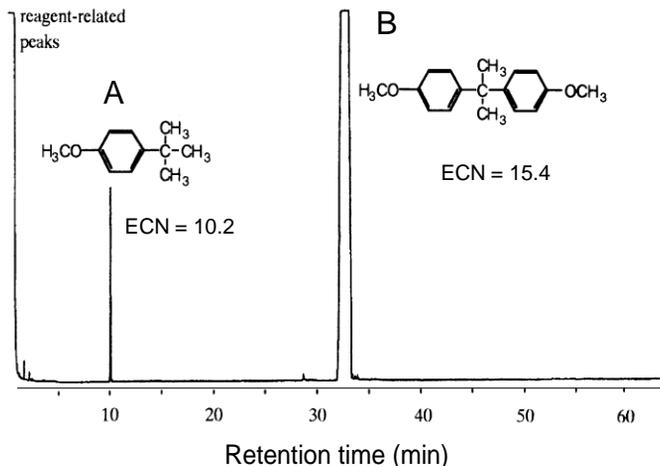


Fig. 1 Pyrograms of a PC sample obtained at 400°C in the presence of TMAH.

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  $\mu\text{m}$   
 Column flow rate: 1.3 ml/min, Detector: FID

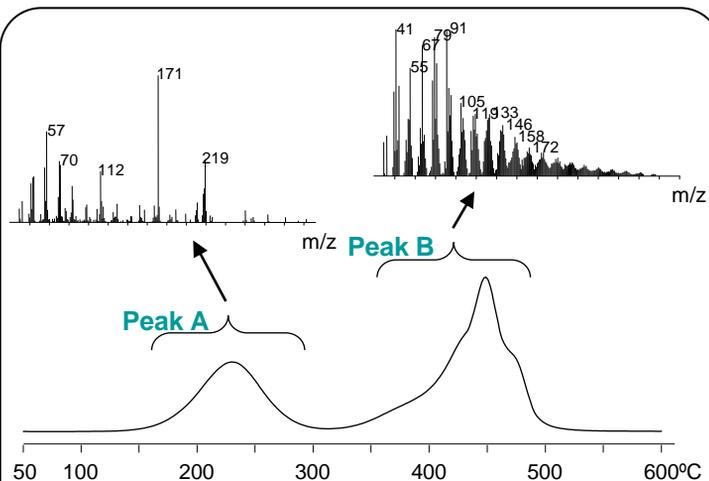
$$DP = \frac{I_B / 15.4}{(I_A / 10.2) / 2} \quad (1)$$

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

**Problem:** 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

**Problem:** How can natural and synthetic fibers be differentiated using evolved gas analysis (EGA)-MS and library search?

**Analysis:** The 21 fiber samples used in this study are shown in Fig. 1. Thermograms of these fibers were obtained by EGA-MS method. Then a library containing the average mass spectra of the main peaks in each thermogram was created using F-Search system. The 21 fibers were differentiated based up 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' sample was then searched using the newly created library. In Fig. 2, the 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. However, candidate 2 has two main peaks and is much different from the unknown. 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 be most likely differentiated using Py-GC/MS.

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

#### • 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), polypropylene, polyethylene, acrylic, polyvinyl chloride, polyvinylidene chloride, polychlal

Fig. 1 Fiber samples used in this study

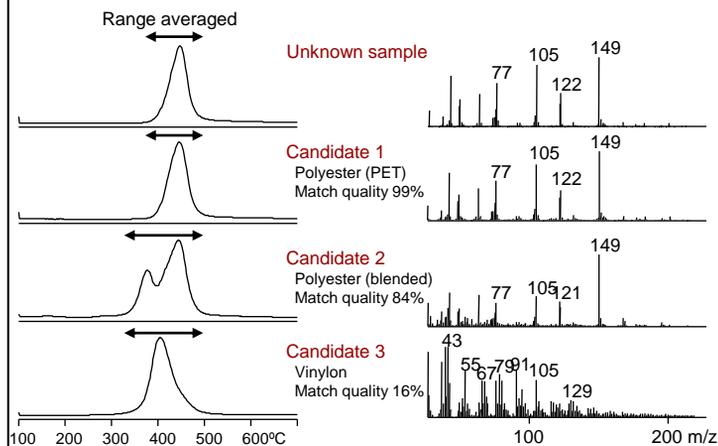


Fig. 2 Comparing the EGA thermogram and average mass spectrum of the "unknown" fiber with the three search candidates with the highest match quality

Pyrolyzer furnace temp.: 100 - 700°C (20°C/min), GC oven temp.: 300°C, 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: ca. 300 µg

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Multi-Shot Pyrolyzer EGA/Py-3030D



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