

Solving Analytical Problems

Version 1.0

using Multi-functional Pyrolyzer[®]

Additives

- Plasticizers
- Releasing agents
- Residual monomers
- Impurities
- Solvents
- 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.



All information subject to change without notice.

Analytical problems and Frontier-Based Solutions

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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.

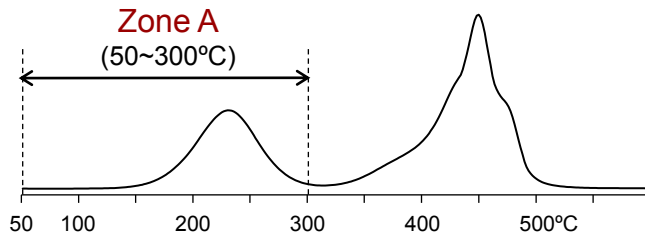


Fig.1 EGA thermogram of NBR

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

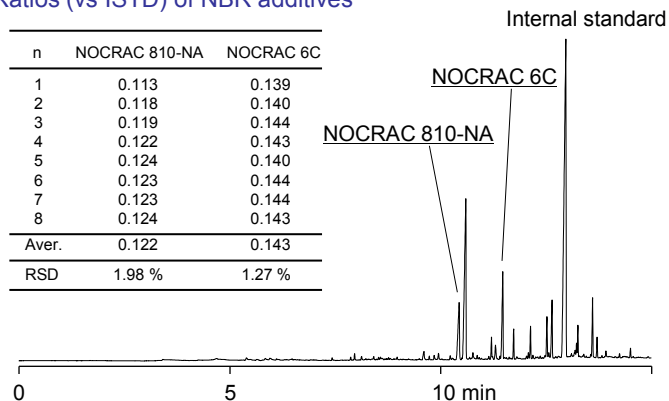


Fig. 2 Chromatogram for Zone A by (TD)-GC/MS analysis

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

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.

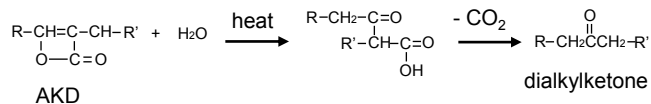


Fig. 1 Formation of ketone by hydrolysis of AKD

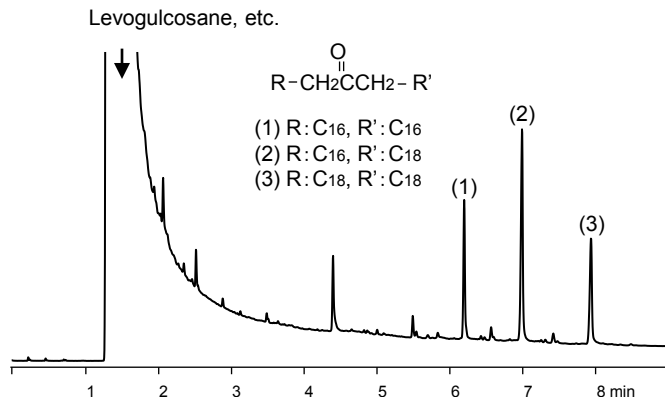


Fig. 2 Analysis of AKD in paper by flash pyrolysis

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

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

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

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

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

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

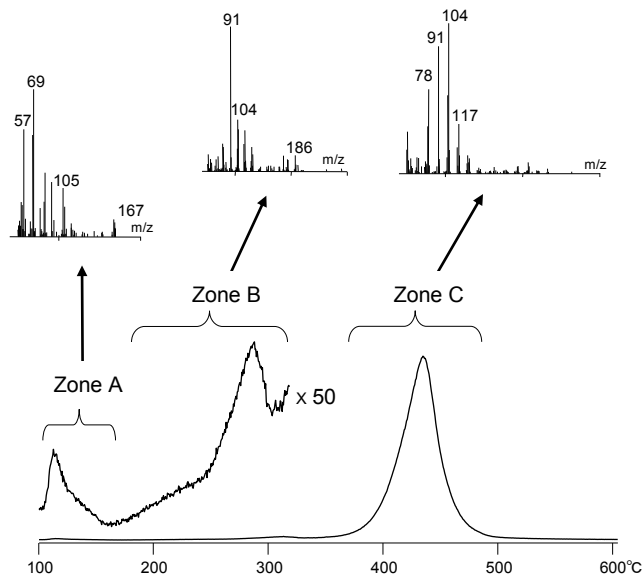


Fig. 1 EGA thermogram of a printer toner and mass spectra of three temperature zones

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

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

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

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

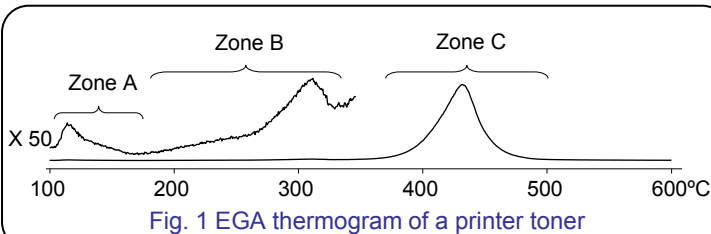


Fig. 1 EGA thermogram of a printer toner

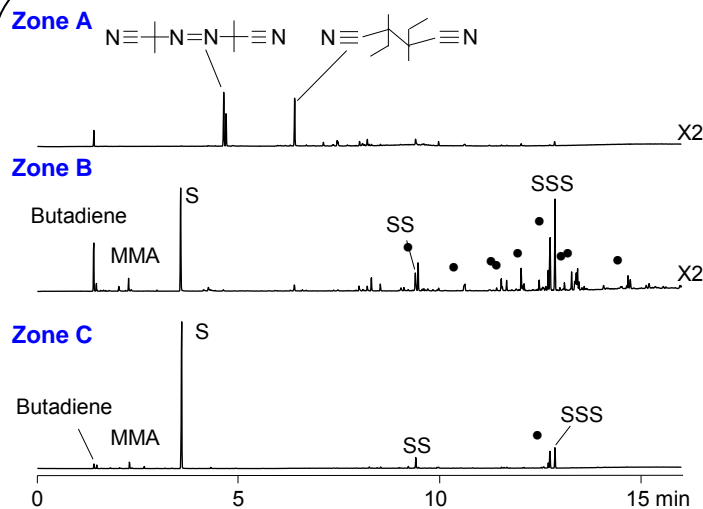


Fig. 2 Chromatogram of each temperature zone of EGA profile

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

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

Problem: 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 |

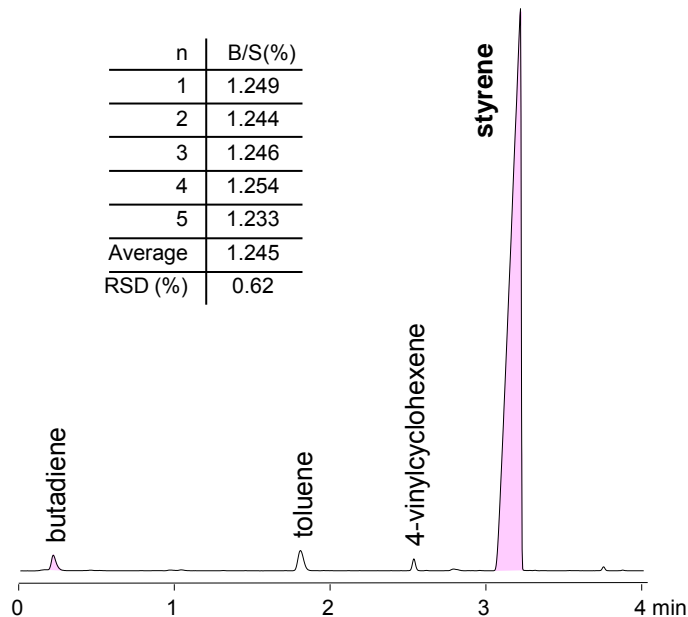


Fig. 1 Pyrogram of HIPS

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

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

Analysis: A piece of polyvinylidene chloride film (0.25 cm², 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.

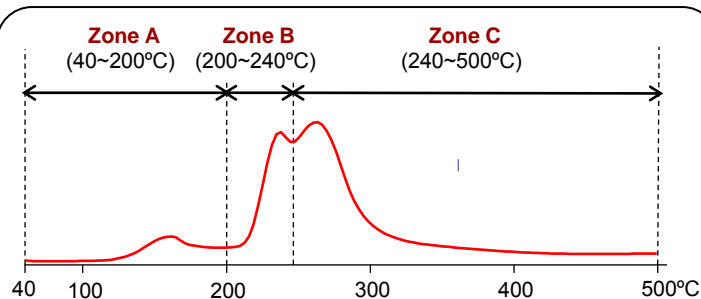


Fig.1 Thermogram of food wrap film

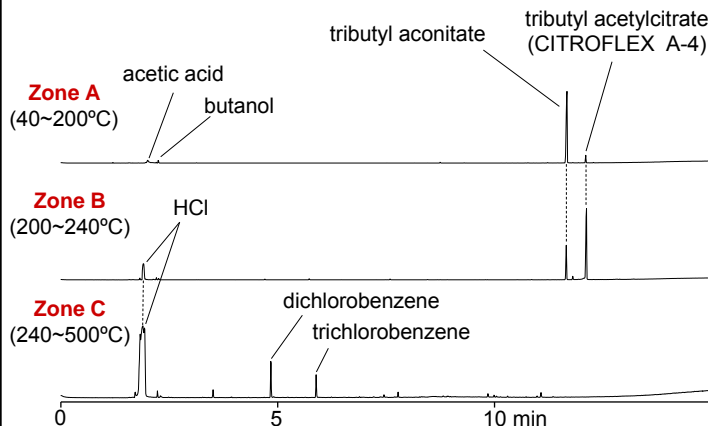


Fig. 2 Chromatograms for Zones A through C by Heart-Cut EGA-GC/MS method

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 C₆, C₉, C₁₂, and C₁₅ derived from pyrolysis of polypropylene, and ε-caprolactam, monomer of nylon-6, were observed.

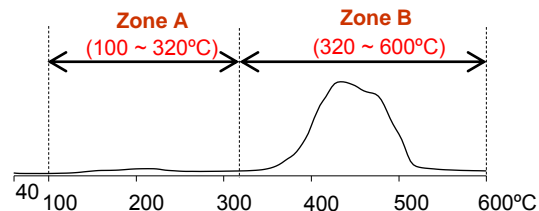


Fig. 1 EGA Profile of Polypropylene + Nylon

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

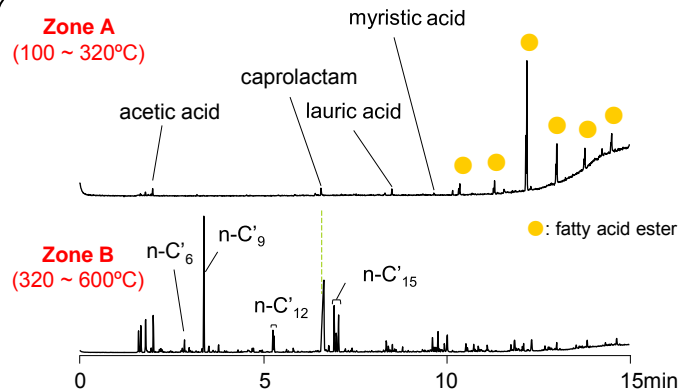


Fig. 2 Analysis Results of Zones A and B of Polypropylene + Nylon

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 |

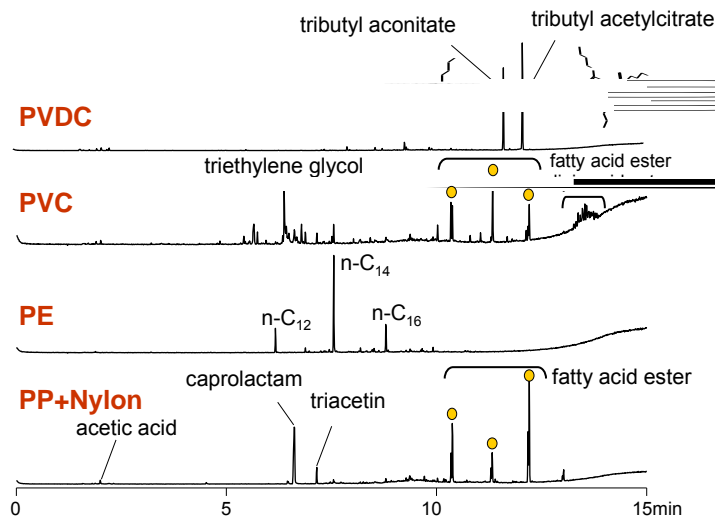


Fig. 1 Chromatograms of evolved gases from food wrap films exposed to 100°C for 10min

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: 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.

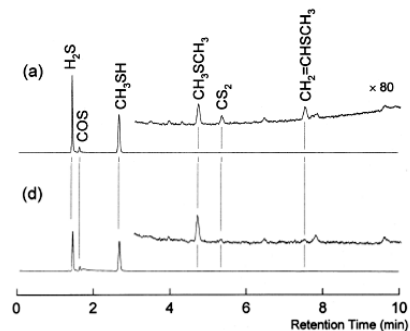


Fig. 1 Pyrograms of photo degraded silk samples at 600°C observed by SCD: (a) not exposed and (b) exposed for 52 days

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 ^{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 CH₃SH

^{b*} from peak intensity of H₂S

^{c*} from peak intensity of CS₂

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

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

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

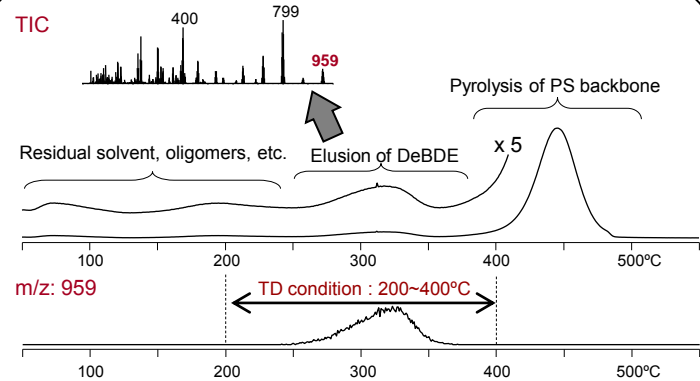


Fig. 1 EGA thermogram of waste plastic

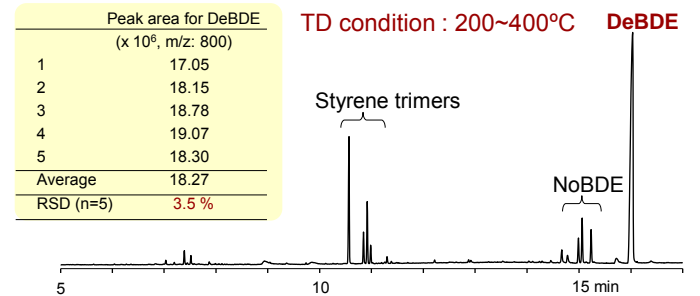


Fig. 2 Chromatogram of waste plastic obtained by (TD)-GC/MS

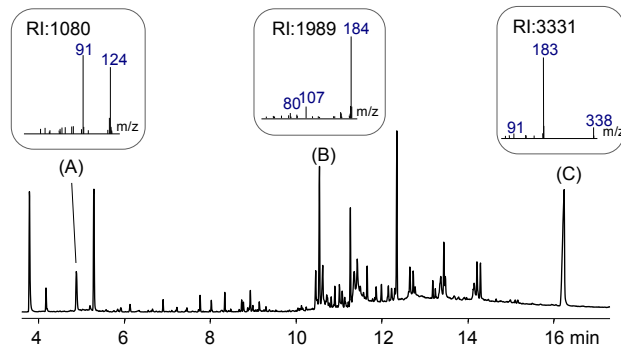
Separation column : UA-PBDE 15M-0.05F
Thermal desorption temp. : 200°C~20°C/min - 400°C

Problem: 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

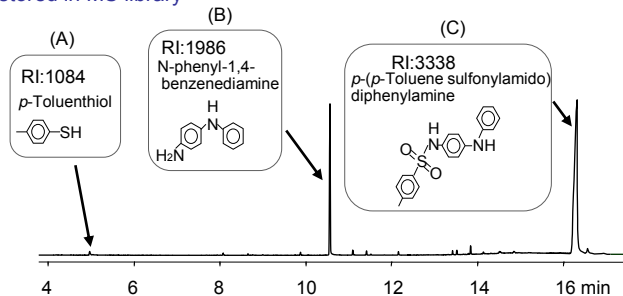


Fig. 1 Chromatogram obtained by (TD)-GC/MS technique

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

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

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

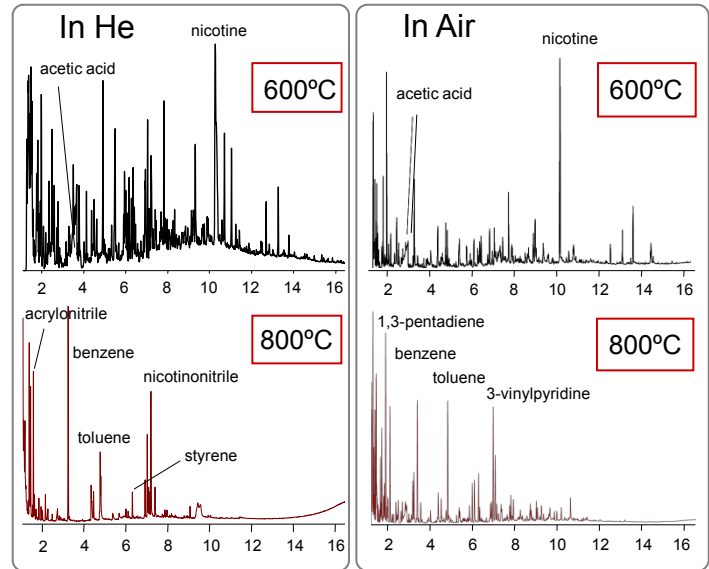


Fig. 1 Pyrograms of tobacco obtained at 600°C and 800°C under air and helium atmosphere

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

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

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

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

Table 1. Use restricted phthalates
(1% upper limit by Directive 2005/84/EC)

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

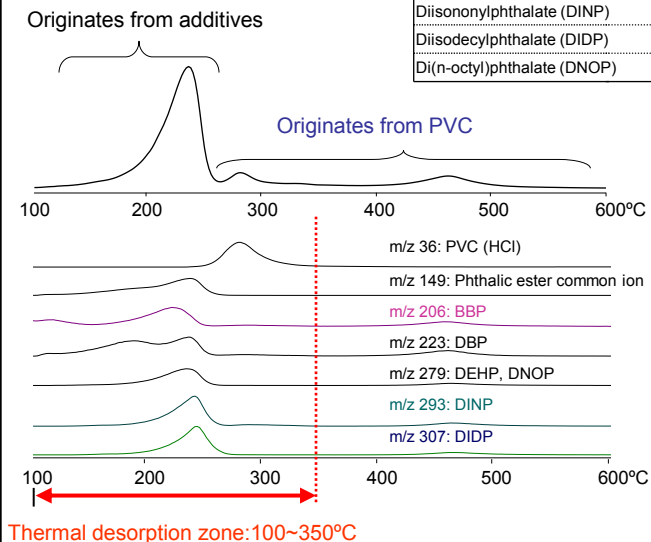


Fig. 1 TIC thermogram and extracted mass chromatograms of PVC, to which 1% each of phthalate was added

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

Problem: 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 100-350°C. The levels of the phthalates were calculated using an absolute area calibration.

Result: Fig. 1 shows a TIC chromatogram obtained by (TD)-GC/MS. DINCH, a non-phthalate plasticizer, was identified as the major component in the 17-18 minute retention window. Compounds having fragment ions m/z 149, 223, 273 were found at 11 and 16 min, and based on the mass spectra and retention times, these peaks are identified as DBP and DEHP. The concentrations of these phthalates are ca. 50 and ca. 300 ppm, respectively. The reproducibility ($n=5$) of the DEHP concentration was 5%RSD for the powder, and 1% for the thin film. The difference between the two can be attributed to the lack of homogeneity of the solid sample.

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

Ca. 50 ppm

ca. 300 ppm

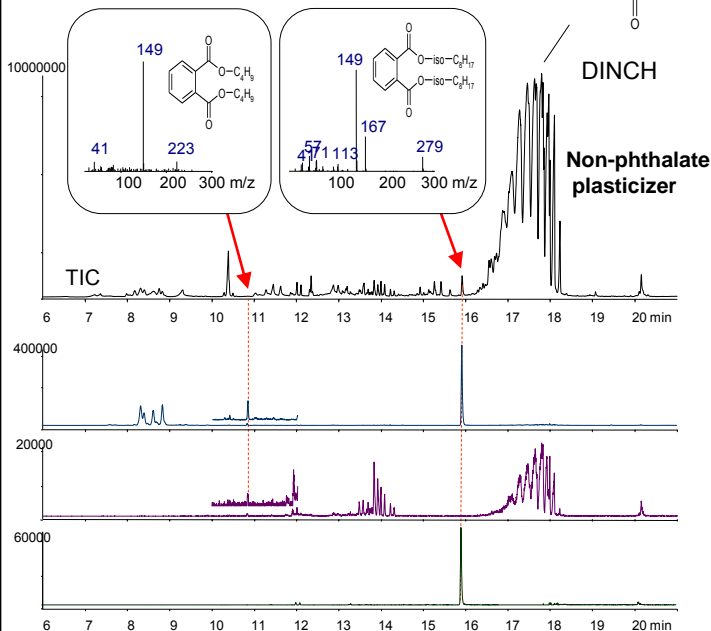
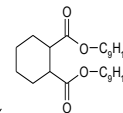


Fig. 1 TIC and extracted ion chromatograms of a PVC sample obtained by (TD)-GC/MS

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

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 300°C. 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.

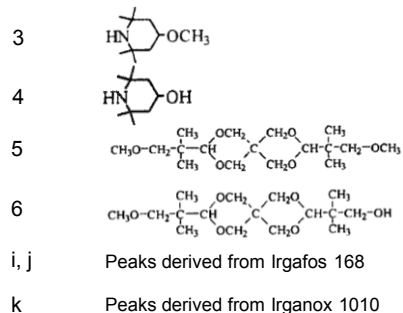
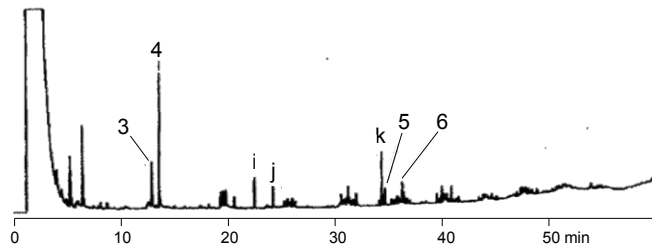
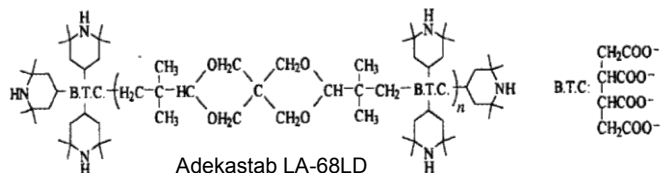
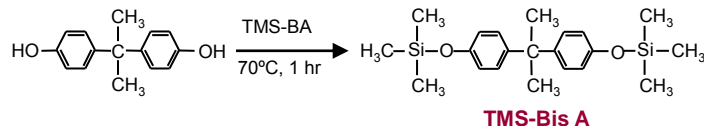


Fig. 1 Typical pyrogram of a polypropylene sample obtained by RTD-GC

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 become 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

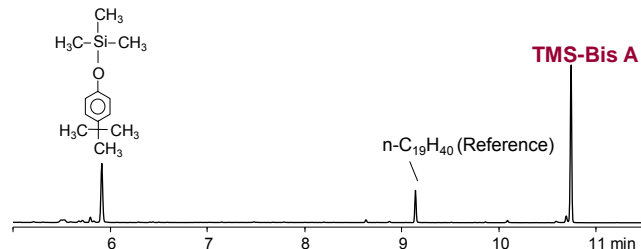


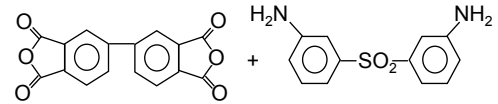
Fig. 1 Chromatogram of a TMS-derivatized PC sample obtained by (TD)-GC/MS

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

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.



(BPDA)

(3,3-DDS)

The first heating process
150°C(30min)

The second heating process
120°C~450°C(3°C/min)

→ Polyamic acid → Polyimide is formed
→ Out-gases are evolved

Fig.1 The synthetic process of polyimide

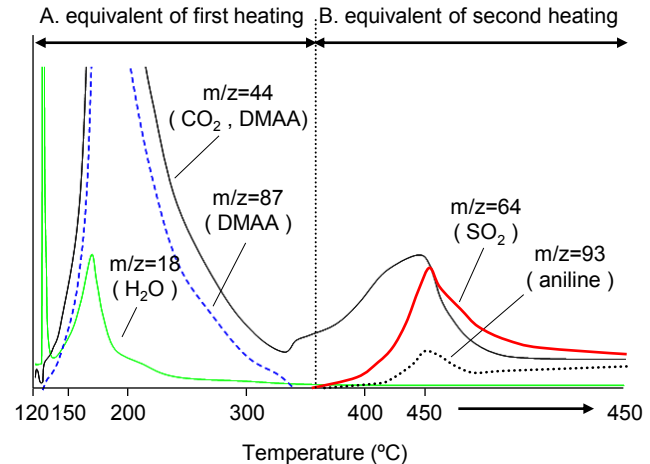


Fig. 2 Thermogram with mass chromatogram in the process of polyimide synthesis

Problem: Is there any simple way to analyze volatile degradation products released from high impact polyethylene (HIPS) during its photo-/thermal/oxidative degradation?

Analysis: Online ultraviolet(UV)/pyrolysis(Py)-GC/MS system can be used to analyze the volatiles. It has a micro UV irradiator equipped with a xenon (Xe) lamp. 10 μ l of dichloromethane solution (2 mg/ml) of HIPS was placed in a sample cup. The sample was irradiated for 1 hr at 60°C under air stream. Volatiles released were cryo-trapped at the head of a separation column. Upon UV irradiation, to drive the volatile products into the column, the sample was heated to 250°C (in He). After the cryo-trap was removed, GC/MS analysis was then started.

Result: Fig. 1 shows the chromatograms of volatiles from HIPS with and without UV irradiation. Upon 1 hour UV irradiation, volatile degradation products originated from PS were observed in addition to 2-propenal. The observation of 2-propenal indicates that a volatile degradation product was indeed generated from butadiene rubber contained in HIPS.

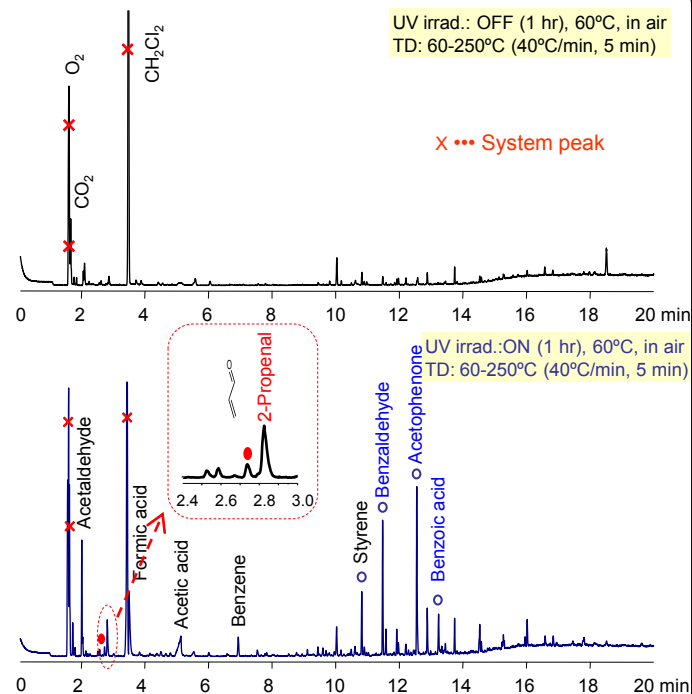


Fig. 1 Chromatograms of volatile degradation products from HIPS generated during UV irradiation obtained by UV/Py-GC/MS

<UV irradiation> Micro UV irradiator : UV-1047Xe, irradiation: 1 hr, furnace temp.: 60°C, 10 ml/min Air, <GC/MS> Separation column: Ultra ALLOY*-1 (polydimethylsiloxane, L=30 m, i.d.=0.25 mm, df=0.5 μ m), GC oven temp.: 40°C(5 min)-240°C(20°C/min), GC injection temp.: 250°C

Problem: Have you found any correlation between micro UV irradiator (Xe lamp) and Xe weather meter in the degradation study of high impact polyethylene (HIPS)?

Analysis: The correlation between the two was investigated by evolved gas analysis (EGA)-MS. HIPS samples were irradiated for 30 min, 1 hour, and 12 hours by the micro UV irradiator at 60°C in air stream, then EGA was performed. In the Xe weather meter experiment, after irradiation of a HIPS plate for 100 or 300 hours, the surface was scraped off and analyzed by EGA.

Result: HIPS sample irradiated for 1 hour by the UV irradiator shows the peak top lowered by 10°C, and the pyrolysis onset temperature lowered from 360 to 300°C. Further, the peak became broader. Also size-exclusion chromatography revealed the molecular weight lowered from 285,000 to 240,000, indicating degradation of the polymer main chain. Also, HIPS sample irradiated for 300 hours by Xe-weather meter shows the peak top lowered by 14°C and the pyrolysis onset temperature lowered from 360 to 280°C. Since both thermograms are almost identical in shape, there is a good correlation between the two.

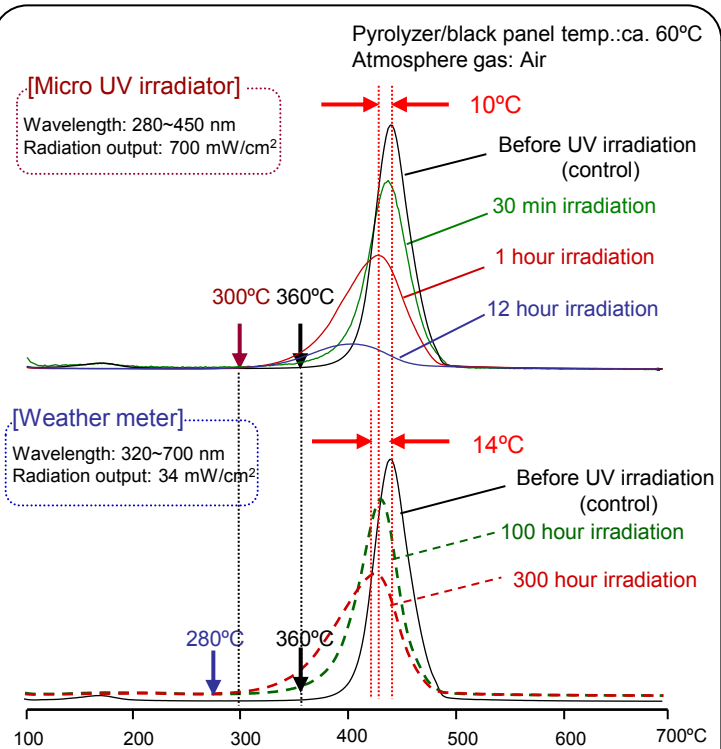


Fig. 1 Thermograms obtained before and after irradiation by UV/Py-GC/MS (top) and Xe weather meter (bottom).

Pyrolysis temp.: 100 - 700°C (20°C/min), GC oven temp.: 300°C
Column: UADTM-2.5N (L=2.5 m, i.d.=0.15 mm)

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