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### *Chapter 3*

## **APPLICATION OF PYROLYSIS - GAS CHROMATOGRAPHY/MASS SPECTROMETRY IN FAILURE ANALYSIS IN THE AUTOMOTIVE INDUSTRY**

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### **ABSTRACT**

The increasing use of polymeric materials, rubbers and chemical fluids, like mineral oils or brake fluids in the automotive industry, demands analytical techniques for the identification of high molecular weight organic compounds. For failure analysis in motor vehicles there is often a lack of information about the component itself, such as chemical composition, temperature resistance, possible contaminants or mechanical properties. The damage range is usually limited and not always homogeneous. Very often only small amounts of samples are available, which may be important for recognizing the cause of damage.

Traditional analytical techniques used for characterization of high molecular weight organic compounds, such as thermal analysis (TA) and Fourier transform infrared spectroscopy (FTIR), are limited or not sufficiently sensitive to demonstrate the change of the structure and the

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resulting dysfunction of used materials. Analytical pyrolysis technique hyphenated to gas chromatography/mass spectrometry (Py-GC/MS) has extended the range of possible tools for characterization of synthetic polymers/copolymers or rubbers. Under controlled conditions at elevated temperature (500 – 1400 °C) in the presence of an inert gas, reproducible decomposition products characteristic for the original sample are formed. Pyrolysis methods eliminate the need for pre-treatment by performing analyses directly on the solid or liquid sample.

This book chapter describes application examples of gas chromatography/mass spectrometry and pyrolysis – gas chromatography/mass spectrometry in failure analysis for the identification of chemical materials like mineral oils and nitrile rubber gaskets. Furthermore, failure cases demanding identification of polymers/copolymers in fouling on the compressor wall of a car air conditioner and identification of fouling on the surface of a bearing race from the automotive industry are demonstrated. The obtained analytical results were then used for troubleshooting and remedial action of the technological process.

## INTRODUCTION

Failure of the structure of materials or components often results in accidents and in hefty compensations. Failure analysis is the process of collecting and analyzing data to determine the cause of a failure and to take action to prevent it from recurring. It is an important discipline in many branches of manufacturing industry, such as the automotive industry. Failure analyses of automotive materials or components help to identify root causes for degradation, malfunction, damage or aging. Various of analytical techniques, like microscopy imaging, scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDX), UV/Vis spectrometry, Fouriertransform infrared spectrometry (FTIR), nuclear magnetic resonance (NMR), time of flight secondary ion mass spectrometry (TOF-SIMS) and others are used for clearing of failure of raw material, manufacturing, function, design or storage errors of various plastic or metal components from the automotive industry.

The increasing use of polymeric materials, rubbers and chemical fluids, like mineral oils or brake fluids in the automotive industry, demands analytical techniques for the identification of high molecular weight organic compounds. For failure analysis in motor vehicles there is often a lack of information about the component itself, such as chemical composition, temperature resistance,

possible contaminants or mechanical properties. The damage range is usually limited and not always homogeneous. Very often only small amounts of samples are available, which may be important for recognizing the cause of damage.

Traditional analytical techniques used for characterization of high molecular weight organic compounds, such as thermal analysis (TA) and Fourier transform infrared spectroscopy (FTIR), are limited or not sufficiently sensitive to demonstrate the change of the structure and the resulting dysfunction of used materials. Analytical pyrolysis technique hyphenated to gas chromatography/mass spectrometry (Py-GC/MS) has extended the range of possible tools for characterization of synthetic polymers/copolymers or rubbers [1-7]. Under controlled conditions at elevated temperature (500 – 1400 °C) in the presence of an inert gas (helium), reproducible decomposition products characteristic for the original sample are formed. Pyrolysis methods eliminate the need for pre-treatment by performing analyses directly on the solid or liquid sample. The pyrolysis unit (pyrolyzer) is directly connected to the injector port of a gas chromatograph (Figures 1-2). Flow of an inert carrier gas, such as helium, flushes the pyrolyzates into the fused silica capillary column, which is installed in the thermostat of the gas chromatograph (GC) (Figure 1). The GC capillary column separates the complex mixture of the organic substances. The chromatographically separated substances are then detected with mass spectrometer (MS) (Figure 1). For detection, the effluent from the GC capillary column is transferred into the ion source near the electron ionisation (EI) filament, which bombards analytes with 70 eV electrons. This is a lot of energy, and it causes organic molecules to readily ionise and form fragment- and molecular ions [8]. The energy of 70 eV is chosen so that across different instrument platforms, for a variety of different analytes, which have different ionization potentials, fragmentation is consistent. Because of this, mass spectral libraries (*e.g.* NIST/EPA/NIH, Wiley, MPW, or Norman Mass Bank) containing thousands of mass spectra for different compounds are available to aid identification of signals for unknown compounds [8]. The MS fragment- and molecular ions can be also identified by self-interpretation of the obtained mass spectra.

The analytical pyrolysis-GC/MS allows the direct analysis of very small solid or liquid polymer/copolymer sample amounts (5-200 µg), without the need of time-consuming sample preparation (sample pre-treatment). The identification of complex mixtures or blends as well as identification of samples with so-called "difficult matrices" is also possible in many cases. Due to these small sample amounts, the investigation of heterogeneous polymers

with a coarse phase or a gradient composition structure (phase separation, poor mixing, etc.) is sophisticated and may lead to great variations in the measuring results. In this case a multiple determination of different positions of the investigated part is essential to achieve a significant image of its composition [7, 9].



Figure 1. Pyrolysis-GC/MS system used in this work equipped with a furnace pyrolyzer *Pyrojector II*<sup>TM</sup> (SGE Analytical Science), control module (SGE Analytical Science), a 7890A gas chromatograph (GC) and a series 5975C quadrupole mass spectrometer (MS) (both from Agilent Technologies).

The applications of the analytical pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) range from research and development of new materials, quality control, characterization and competitor product evaluation, medicine, biology and biotechnology, geology, airspace, environmental analysis to forensic purposes or conservation and restoration of cultural heritage. These applications cover analysis and identification of polymers/copolymers and additives in components of automobiles, tires, packaging materials, textile fibres, coatings, adhesives, half-finished products for electronics, paints or varnishes, lacquers, leather, paper or wood products, food, pharmaceuticals, surfactants and fragrances [2-3].



Figure 2. View of the furnace pyrolyzer *Pyrojector II*<sup>TM</sup> (SGE Analytical Science) connected to the injection port of the gas chromatograph (GC).

For more than ten years, our laboratory has been involved in the projects from the area of failure analysis in the automotive industry by using the analytical pyrolysis-gas chromatography/mass spectrometry. The high success rate in solution of problems and the satisfaction of our clients has convinced us, that this analytical technique is well suited for the failure analysis in the automotive industry [7, 9].

This book chapter describes application examples of the gas chromatography/mass spectrometry (GC/MS) and analytical pyrolysis – gas chromatography/mass spectrometry (Py-GC/MS) for the identification of chemical materials like mineral oils, and nitrile-butadiene rubbers (NBR) used in the automotive industry. Furthermore, failure analysis cases demanding identification of polymers/copolymers in fouling on the wall of a car air conditioner, and identification of fouling on the surface of a bearing race from the automotive industry are demonstrated. The obtained analytical results were then used for troubleshooting and remedial action of the technological process.

## EXPERIMENTAL

### Materials and Apparatus

Approximately 100-200 µg of the solid sample of rubber or fouling from the automotive part was inserted without further preparation into the bore of the pyrolysis solids-injector and then placed with the plunger on the quartz wool of the quartz tube of the furnace pyrolyzer *Pyrojector II*<sup>TM</sup> (SGE Analytical Science, Melbourne, Australia). The pyrolyzer was operated at constant temperature of 700 °C. The pressure of helium carrier gas at the inlet to the furnace was 95 kPa. Pyrolysis-GC/MS measurements were made by using two apparatuses. In the first apparatus (1), the pyrolyzer was connected to a *Trace 2000* gas chromatograph (ThermoQuest/CE Instruments, Milan, Italy) with a quadrupole mass spectrometer *Voyager* (ThermoQuest/Finnigan, MassLab Group, Manchester, UK) operated in electron impact ionization (EI) mode. The fused silica GC capillary column *Elite-5ms* 60 m long, 0.25 mm I.D., 0.25 µm film thickness (PerkinElmer, Shelton, CT, U.S.A.) was used. The gas chromatographic conditions were as follow: programmed temperature of the capillary column from 60 °C (1 min hold) at 2.5 °C min<sup>-1</sup> to 100 °C and then 10 °C min<sup>-1</sup> to 280 °C (20 min hold at 280 °C). The temperature of the split/splitless injector was 250 °C and the split flow was 10 cm<sup>3</sup> min<sup>-1</sup>. Helium, grade 5.0 (Westfalen AG, Münster, Germany) was used as a carrier gas. The programmed pressure of the carrier gas from 70 kPa (1min hold) at 1 kPa/min to 110 kPa (hold to the end of analysis) was used. The transfer line temperature was 280 °C. The MS EI ion source temperature was kept at 250 °C. The ionization occurred with a kinetic energy of the impacting electrons of 70 eV. The current emission of the rhenium filament was 150 µA. The MS detector voltage was 350 V. Mass spectra and reconstructed chromatograms

(total ion current [TIC]) were obtained by automatic scanning in the mass range  $m/z$  35 - 455 u. Pyrolysis-GC/MS data were processed with the *Xcalibur* software (ThermoQuest) and the *NIST 05* mass spectral library.

In the second apparatus (2), the pyrolyzer was connected to a 7890A gas chromatograph with a series 5975C quadrupole mass spectrometer (Agilent Technologies Inc., Santa Clara, CA, U.S.A.) operated in electron impact ionization (EI) mode (Fig. 1). The fused silica GC capillary column 60 m long, 0.25 mm I.D. with *DB-5ms* stationary phase, film thickness 0.25  $\mu\text{m}$  (J&W Scientific, Folsom, CA, U.S.A.) was used. Helium, grade 5.0 (Westfalen AG) was used as a carrier gas. The gas chromatographic conditions were as follow: programmed temperature of the capillary column from 75 °C (1 min hold) at 7 °C  $\text{min}^{-1}$  to 280 °C (hold to the end of analysis) and programmed pressure of helium from 122.2 kPa (1 min hold) at 7 kPa  $\text{min}^{-1}$  to 212.9 kPa (hold to the end of analysis). The temperature of the split/splitless injector was 250 °C and the split ratio was 20:1. The transfer line temperature was 280 °C. The MS EI ion source temperature was kept at 230 °C. The ionization occurred with a kinetic energy of the impacting electrons of 70 eV. The quadrupole temperature was 150 °C. Mass spectra and reconstructed chromatograms (total ion current) were obtained by automatic scanning in the mass range  $m/z$  35 - 750 u. Pyrolysis-GC/MS data were processed with the *ChemStation* software (Agilent Technologies) and the *NIST 05* mass spectral library.

For direct GC/MS analyses, solutions of 100  $\text{mg}/\text{cm}^3$  of mineral oil (Motul Deutschland, Cologne, Germany) in *n*-heptan and the same GC/MS apparatus (2) though without pyrolyzer were used. The fused silica GC capillary column 30 m long, 0.25 mm I.D. with *DB-5ms* stationary phase, film thickness 0.25  $\mu\text{m}$  (J&W Scientific, Folsom, CA, U.S.A.) was used. Helium, grade 5.0 (Westfalen AG) was used as a carrier gas at constant flow of 1  $\text{cm}^3/\text{min}$ . The gas chromatographic conditions were as follow: programmed temperature of the capillary column from 150 °C (1 min hold) at 3 °C  $\text{min}^{-1}$  to 300 °C (hold 70 min). The temperature of the split/splitless injector was 250 °C and the split ratio was 15:1. The transfer line temperature was 300 °C. The MS EI ion source temperature was kept at 230 °C. The ionization occurred with a kinetic energy of the impacting electrons of 70 eV. The quadrupole temperature was 150 °C. Mass spectra and reconstructed chromatograms (total ion current) were obtained by automatic scanning in the mass range  $m/z$  30 - 850 u. The solvent delay was 9 minutes. Pyrolysis-GC/MS data were processed with the *ChemStation* software (Agilent Technologies).

For the identification of the investigated mineral oils, the ASTM<sup>®</sup> D2887 calibration mix (Sigma-Aldrich, Supelco, Bellefonte, PA, U.S.A.) and the *NIST 05* mass spectral library were used.

## RESULTS AND DISCUSSION

### Case Study 1 – Identification of the Composition of Motor Vehicle Oils

The modern engine lubricant is a carefully designed blend of base oils and performance enhancing additives, such as pour point depressants, antioxidants, dispersants and detergents [10]. The base lubricating oils can be roughly divided into three major classes: all-natural oils, semi-synthetic oils, and fully synthetic oils. All-natural base oils are traditional petroleum oils made by the refinement of crude oil. During the refinement process, paraffin waxes are typically removed from the oils, and these waxes can be hydrocracked to produce semi-synthetic oils. The fully synthetic oils are generally either long chain esters or low molecular weight polyalphaolefins (PAO) [10]. Mineral oil analysis is a widely used application that is ideal for gas chromatography (GC) or GC/MS. Fast screening of the sample is important to characterize the type of mineral oil involved [11].

In this case study, in order to find differences between the chemical compositions of four motor vehicle oils, the samples were identified by direct GC/MS analysis without previous pyrolysis. Fig. 3 (A-D) shows the obtained GC/MS chromatograms (TIC, total ion current) of the investigated mineral oils. For the identification of compounds, the ASTM<sup>®</sup> D2887 calibration mix and the *NIST 05* mass spectral library were used. Fig. 4 shows the obtained TIC of the *n*-alkanes identified in the calibration mix. The retention data of the separated compounds from the calibration mix (Fig. 4) has allowed the identification of *n*-alkanes in oil samples. In the first oil sample (Fig. 3 A) a mixture of *n*-alkanes from C<sub>24</sub>H<sub>50</sub> (*n*-tetracosane) up to C<sub>36</sub>H<sub>74</sub> (*n*-hexatriacontane) was detected. It was found that the investigated oil sample included also synthetic esters, like vinyl caprylate (P 534) (retention time  $t_R$  = 48.36 min), glyceryl tridecanoate (P 1186) (retention time  $t_R$  = 52.06 min) and others (retention time  $t_R$  = 56.43 min and  $t_R$  = 62.23 min). Additionally, in the oil sample diphenyloctylamin (P 524) (retention time  $t_R$  = 28.69 min) was detected. The total content of the determined organic additives in the first oil sample was about 15.5%.



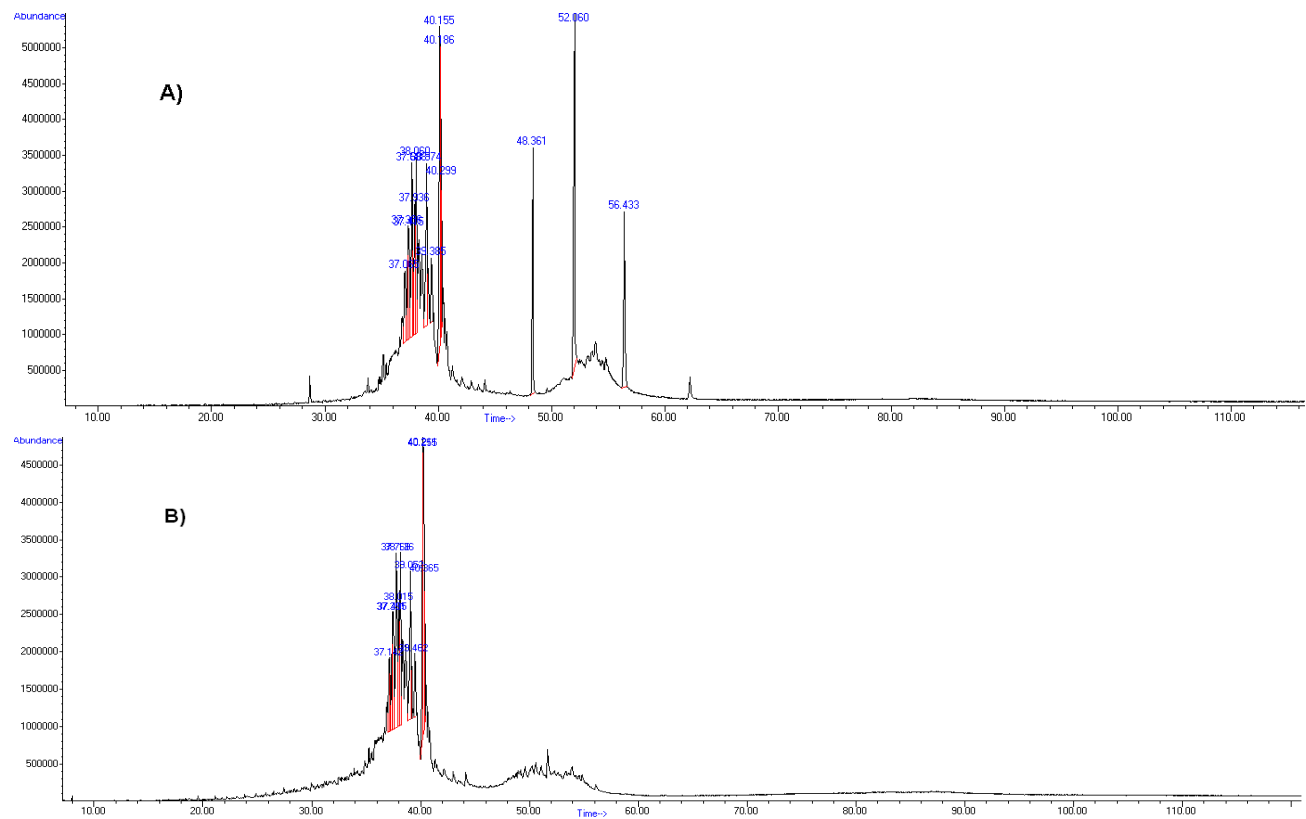


Figure 3. (Continued).

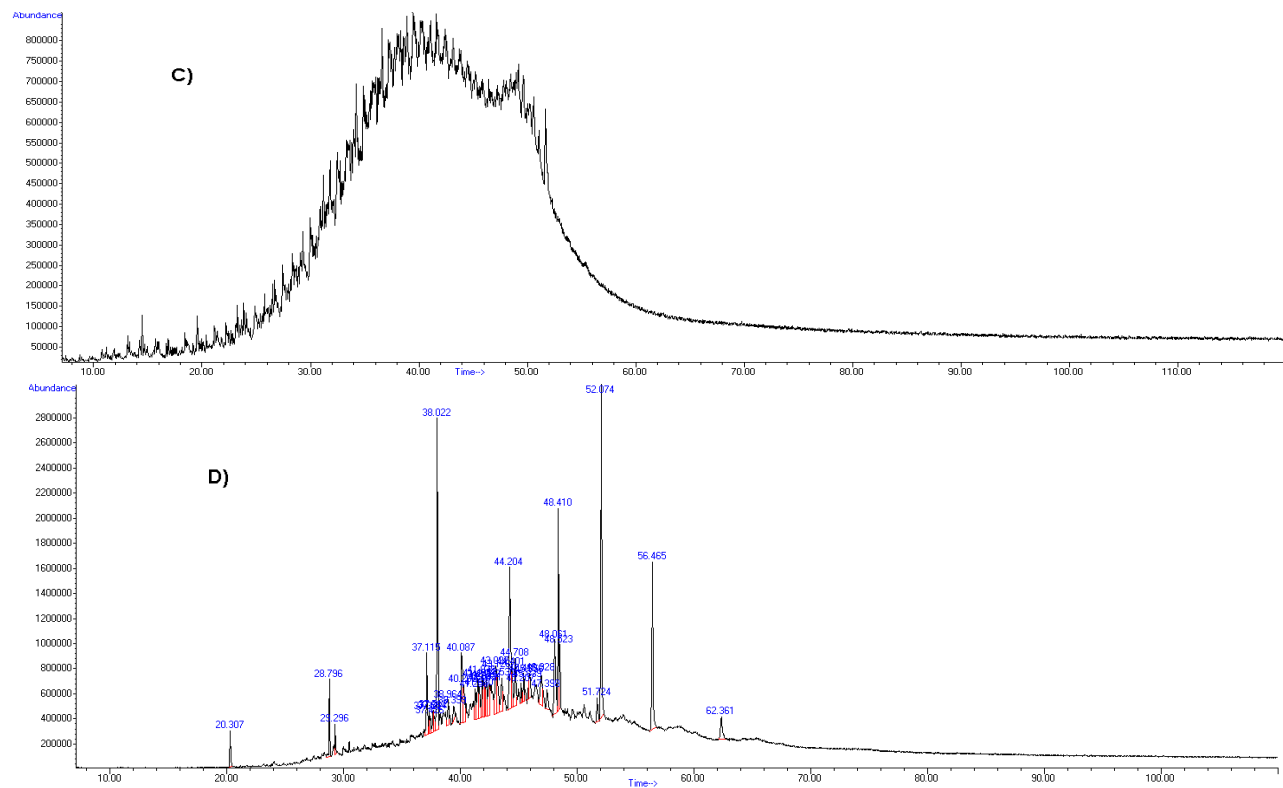


Figure 3. GC/MS chromatograms (TIC, total ion current) of the investigated motor oils. For analytical conditions, see Experimental (direct GC/MS analyses).

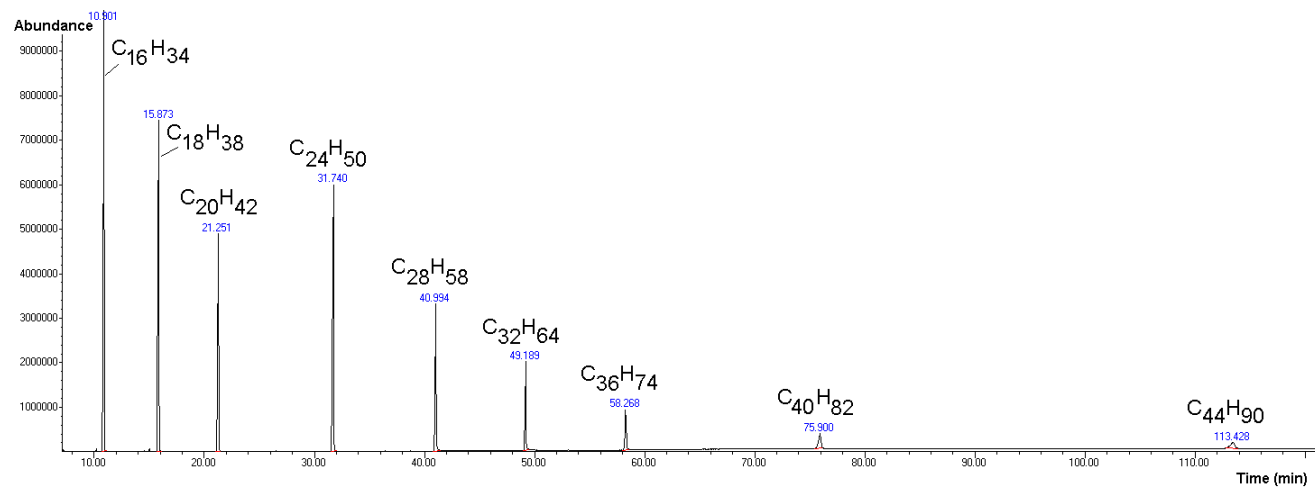


Figure 4. GC/MS chromatogram (TIC, total ion current) of the ASTM<sup>®</sup> D2887 calibration mix. For analytical conditions, see Experimental (direct GC/MS analyses). Peak identification:  $C_{16}H_{34}$  – *n*-hexadecane,  $C_{18}H_{38}$  – *n*-octadecane,  $C_{20}H_{42}$  – *n*-eicosane,  $C_{24}H_{50}$  – *n*-tetracosane,  $C_{28}H_{58}$  – *n*-octacosane,  $C_{32}H_{66}$  – *n*-dotriacontane,  $C_{36}H_{74}$  – *n*-hexatriacontane,  $C_{40}H_{82}$  – *n*-tetracontane,  $C_{44}H_{90}$  – *n*-tetratetracontane.

In the second oil sample (Figure 3 B) and in the third oil sample (Fig. 3 C) no organic additives were detected. The oils consist only of *n*-alkanes from  $C_{20}H_{42}$  (*n*-eicosane) up to  $C_{36}H_{74}$  (*n*-hexatriacontane) in the oil sample B, and *n*-alkanes from  $C_{16}H_{34}$  (*n*-hexacosane) up to  $C_{38}H_{78}$  (*n*-octatriacontane) in the oil sample C, respectively.

In the fourth oil sample (Figure 3 D) however, a mixture of *n*-alkanes from  $C_{23}H_{48}$  (*n*-tricosane) up to  $C_{38}H_{78}$  (*n*-octatriacontane), diphenyloctylamin (P 524) (retention time  $t_R = 28.80$  min), antioxidant 4,4'-methylene-bis(2,6-di-*tert*-butylphenol) (E 702) (retention time  $t_R = 38.02$  min), and synthetic esters vinyl caprylate (P 534) (retention time  $t_R = 48.41$  min), and glyceryl tridecanoate (P 1186) (retention time  $t_R = 52.07$  min) were identified. Other additives (retention time  $t_R = 20.31$  min, 29.30 min, 37.11 min, 44.20 min, 56.46 min, and 62.36 min, respectively) could not be definitely identified. The total content of the determined organic additives in the fourth oil sample was about 31%.

The developed GC/MS method has allowed the classification and identification of the investigated motor oils.

## Case Study 2 – Identification of O-Ring Seals from the Automotive Industry

Commonly used rubbers in the automotive industry are natural rubber (NR, polyisoprene), synthetic polyisoprene (IR), polybutadiene (BR), styrene-butadiene copolymers (SBR) and nitrile rubber (NBR). Nitrile rubber [poly(acrylonitrile-*co*-butadiene)] (Figure 5) is a copolymer containing 15 – 50% acrylonitrile, manufactured by emulsion polymerisation of acrylonitrile and 1,3-butadiene. It was invented at roughly the same time as SBR (near the end of the 1920s), as a substitute for natural rubber [5, 7]. The major applications for this material are in areas requiring oil and solvent resistance. The largest market for nitrile rubber is in the automotive industry because of its solvent and oil resistance. Major end uses are for hoses, fuel lines, O-rings, gaskets and seals.

In blends with poly(vinyl chloride) (PVC) and poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS), nitrile rubber acts as an impact modifier. Some nitrile rubber is sold in latex form for the production of grease-resistant tapes, gasketing material and abrasive papers [5]. The study of rubbers is the oldest application of the analytical pyrolysis - GC/MS technique.

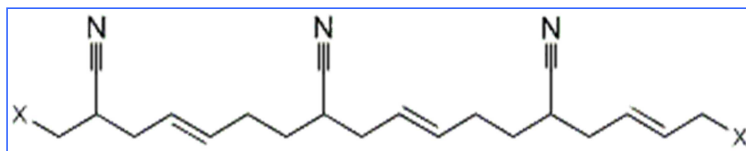


Figure 5. Chemical structure of poly(acrylonitrile-*co*-butadiene) (NBR).

In the following failure analysis case four O-ring seals from the automotive industry were investigated by analytical pyrolysis – GC/MS at 700 °C, because two of which (samples 2 and 4) other properties have shown. The detailed identification of the pyrolysis products of the investigated O-ring seals by using the *NIST 05* mass spectral library is summarized in Table 1. The material of all four samples was identified as poly(acrylonitrile-*co*-butadiene) (nitrile rubber, NBR) based on the decomposition products like acetonitrile, acrylonitrile, methacrylonitrile, benzene, toluene, styrene, benzonitrile, methylbenzonitrile and benzylnitrile (Fig. 6 and Table 1).

The main feature of pyrolysis of nitrile rubber is the formation of the monomers 1,3-butadiene (retention time  $t_R = 8.84$  min) and acrylonitrile (retention time  $t_R = 9.05$  min).

The presence of benzonitrile (retention time  $t_R = 13.14$ min) in pyrograms is also characteristic for the pyrolysis of nitrile rubber [5, 12-14]. In the pyrograms of the pyrolysis products of O-ring seals (Fig. 6) however, quantitative differences between the proportion of styrene and benzonitrile were found.

The peak area ratio styrene/benzonitrile in O-ring seals 1 and 3 was calculated as 1:2, whereas in O-ring seals 2 and 4 as 1:1. Based on the results, it can be assumed that the content of the monomer acrylonitrile in NBR seals 1 and 3 differs from the content of acrylonitrile in NBR seals 2 and 4.

The observed method differences by using pyrolysis-GC/MS in the composition of the pyrolysates could have an effect on the properties of the NBR rubbers.

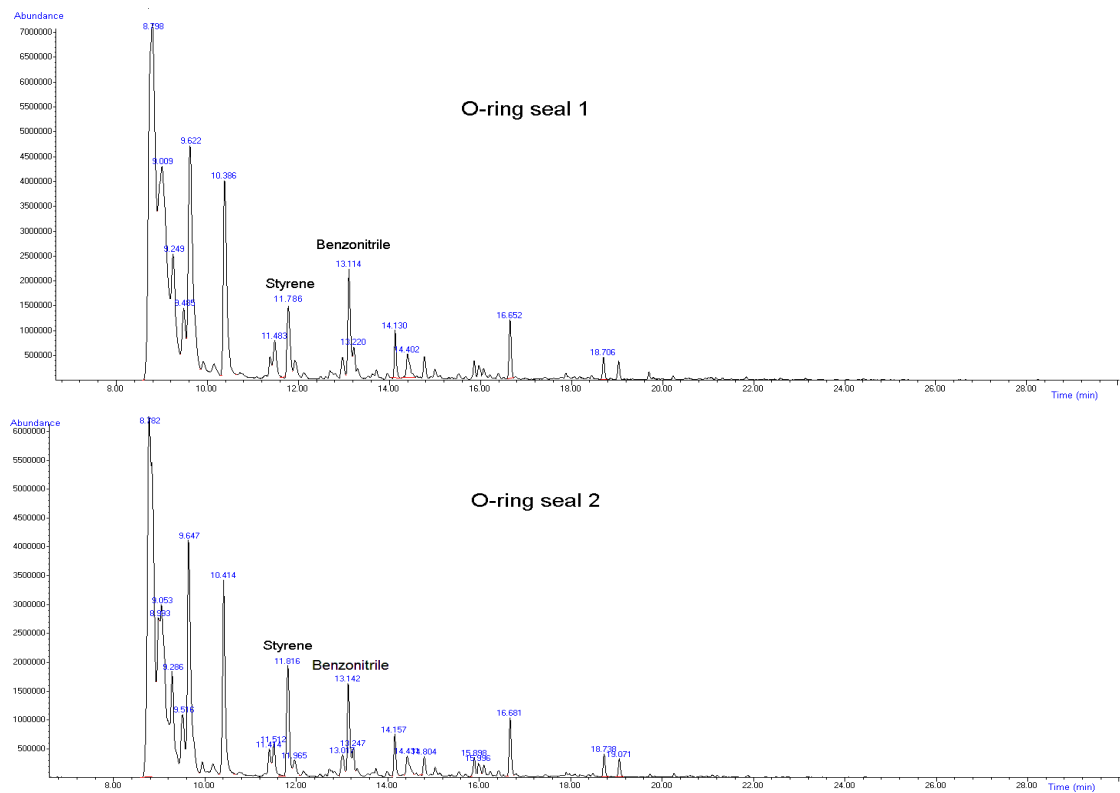


Figure 6. (Continued).

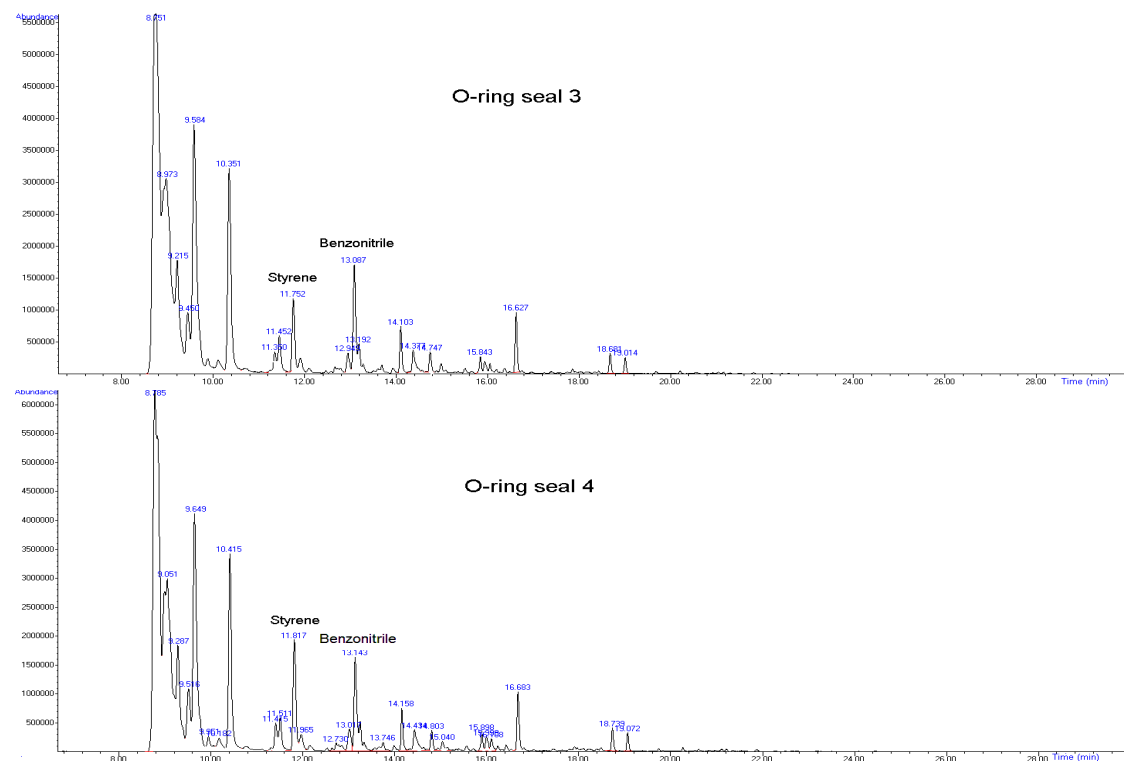


Figure 6. Pyrolysis – GC/MS chromatograms (pyrograms) of the investigated O-ring seals at 700 °C. Analytical conditions as in Experimental (second apparatus).

**Table 1. Identification of the pyrolysis products of the investigated O-ring seals (NBR) at 700 °C**

Retention time, $t_R$ (min)*	Pyrolysis product
8.77	Propylene
8.84	Butene/1,3-butadiene
8.98	Acetonitrile
9.05	Acrylonitrile
9.29	Methacrylonitrile
9.65	Benzene
10.41	Toluene
11.41	Ethylbenzene
11.51	<i>p</i> -Xylene
11.82	Styrene
13.02	Aniline
13.14	Benzonitrile
13.25	Propenylbenzene
13.75	<i>o</i> -Methylstyrene
14.16	Indene
14.43	2-Methylbenzonitrile
14.80	4-Methylbenzonitrile
15.55	Benzyl nitrile
16.68	Naphthalene
18.74	Methylnaphthalene isomer
19.07	Methylnaphthalene isomer

\* Retention times taken from the pyrogram of the O-ring 2 sample.

### Case Study 3 – Identification of the Composition of Sludge on the Surface of the Compressor Wall from a Car Air Conditioner

In the following case, sludge on the surface of the compressor wall from a car air conditioner was identified. Fig. 7 shows a magnified view of the sludge allocation on the surface of the investigated component, while Fig. 8 shows the pyrogram of the examined sludge pyrolyzed at 700 °C. The pyrolysis products, identified by using the mass spectral library *NIST 05*, are summarized in Table 2. Based on the identified decomposition products (Figure 8 and Table 2), the sludge was identified as a mixture of mineral oil and epoxy resin on bisphenol A basis.



**Table 2. Identification of the pyrolysis products of sludge from a car air conditioner pyrolysed at 700 °C**

Retention time, $t_R$ (min)	Pyrolysis product
7.05	Propylene
7.13	Butene/1,3-butadiene
7.29	1-Pentene
7.59	1-Hexene
8.04	Benzene
8.14	1-Heptene
8.95	Toluene
9.06	1-Octene
10.07	Pentadecanoic acid
10.39	1-Nonene
10.60	Styrene
11.75	Phenol
12.04	1-Decene
12.44	Benzo[ <i>a</i> ]furane
13.14	<i>o</i> -Cresol
13.50	<i>p</i> -Cresol
13.84	1-Undecene
15.71	1-Dodecene
16.42	<i>p</i> -Isopropylphenol
17.69	1-Tridecene
17.94	<i>p</i> -Isopropenylphenol
19.71	1-Tetradecene
21.72	1-Pentadecene
22.65	1,2-Diphenylethylene
23.67	1-Hexadecene
25.56	1-Heptadecene
28.69	3-Stilbenol
28.96	<i>p</i> -Cumylphenol
29.32	Hexadecanitrile
32.79	Heptadecanitrile
34.44	Bisphenol A

The presence of *n*-alkenes  $C_3H_6$  (propylene) up to  $C_{17}H_{34}$  (1-heptadecene) in pyrolysate is characteristic for the pyrolysis of mineral oil (motor oil). The peaks of aromatics, like benzene, toluene and styrene, as well as the peaks of phenolic compounds, like phenol, cresols, *p*-isopropylphenol, *p*-isopropenylphenol, *p*-cumylphenol and bisphenol A, indicate the presence of the epoxy resin on bisphenol A basis in the investigated sludge.

The obtained analytical results were then used for troubleshooting with the customer.

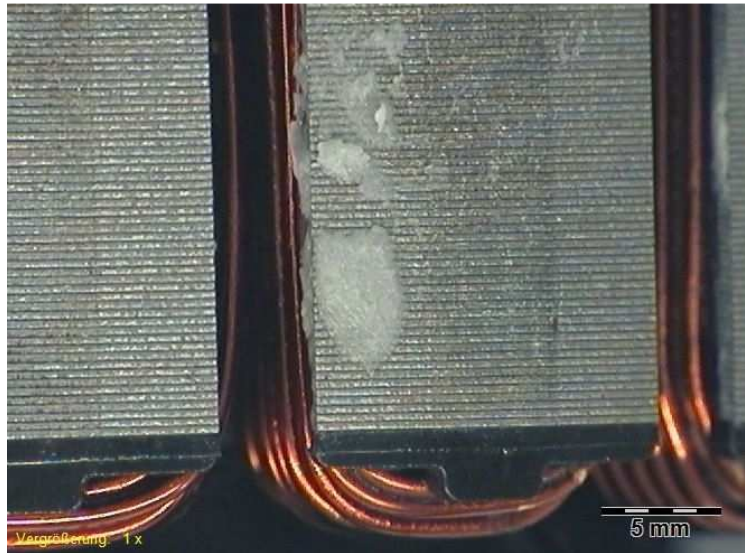
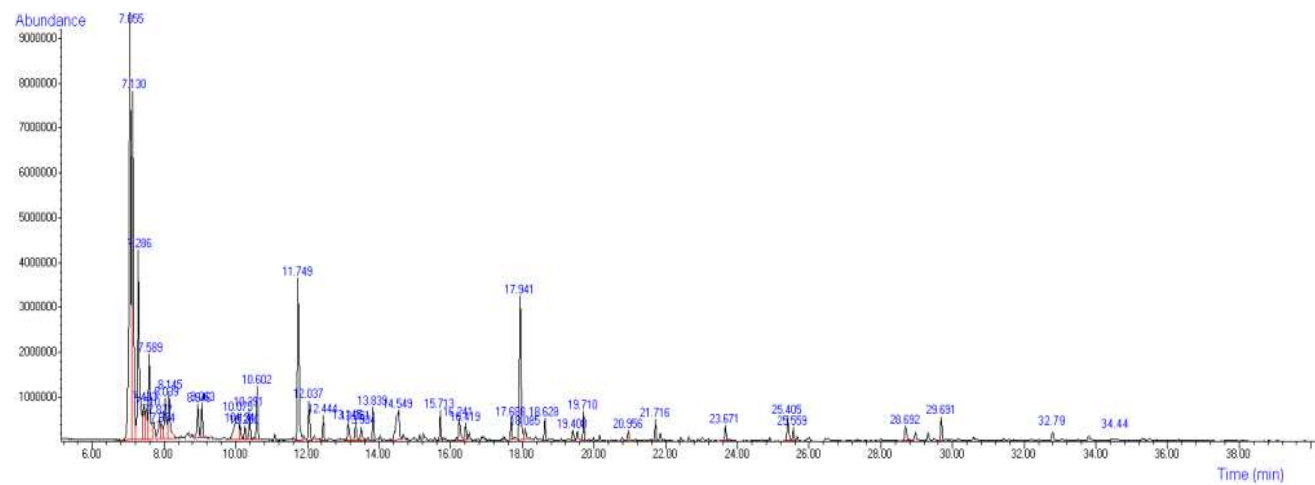


Figure 7. View of the sludge allocation on the surface of the investigated car air conditioner.

#### **Case Study 4 – Identification of the Composition of fouling on the Surface of a Bearing Race**

In the following case the composition of fouling on the internal surface of a bearing race from a car was to identify. The sampling was done by rubbing the affected surface with quartz glass wool and subsequent pyrolysis of the impregnated glass wool at 700 °C followed by GC/MS analysis. Fig. 9 shows the obtained pyrolysis-GC/MS chromatogram. The fouling of the bearing race was identified with reference materials and with the help of the *NIST 05* mass spectra library as a mixture of mineral oil, styrene-butadiene rubber (SBR), polyamide 6.6 (PA 6.6, Nylon), and epoxy resin.



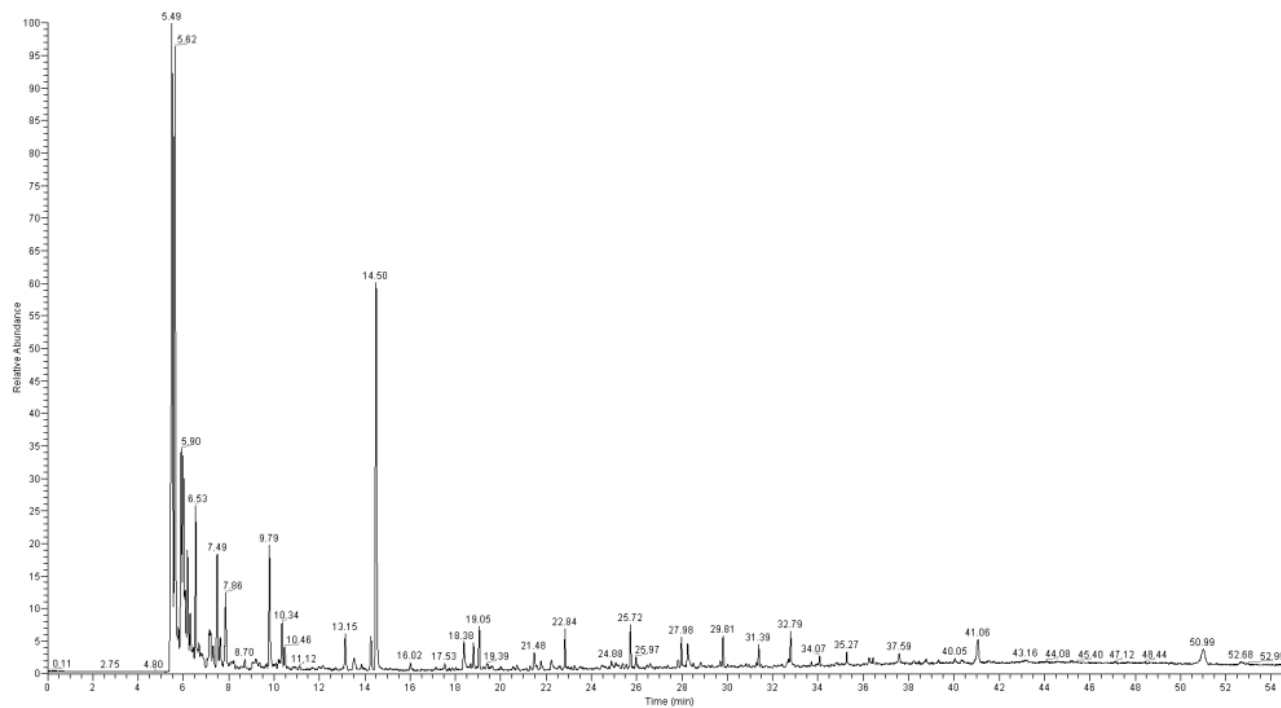


Figure 9. Pyrolysis – GC/MS chromatogram (pyrogram) of fouling on the internal surface of a bearing race from a car pyrolysed at 700 °C. Analytical conditions as in Experimental (first apparatus).

The pyrolysis products of the investigated fouling as well as their origin are summarized in Table 3. The presence of *n*-alkenes C<sub>3</sub>H<sub>6</sub> (propene) up to C<sub>20</sub>H<sub>40</sub> (1-eicosene) in pyrolysate is characteristic for the pyrolysis of mineral oil (motor oil). The peaks of butene/1,3-butadiene, benzene, toluene, ethylbenzene, *o*-xylene, styrene and  $\alpha$ -methylstyrene indicate the presence of styrene-butadiene rubber (SBR). The peak of cyclopentanone (retention time  $t_R = 10.46$  min) is characteristic for the pyrolysis of polyamide 6.6 (PA 6.6, Nylon), while the peaks of phenol and *p*-isopropenylphenol could be generated from the epoxy resin (Fig. 9 and Table 3). The identified materials could be then assigned to the corresponding car components. The obtained analytical results were then used for troubleshooting with the customer.

**Table 3. Identification of the pyrolysis products of fouling on the internal surface of a bearing race from a car pyrolysed at 700 °C**

Retention time, $t_R$ (min)	Pyrolysis product	Origin
5.49	Propylene	Mineral oil
5.62	Butene/1,3-butadiene	Mineral oil, SBR
5.90	1-Pentene	Mineral oil
5.99	Pentadiene	Mineral oil
6.18	Cyclopentadiene	Mineral oil
6.53	1-Hexene	Mineral oil
7.14	Cyclohexadiene	Mineral oil
7.49	Benzene	SBR
8.70	1-Heptene	Mineral oil
9.79	Toluene	SBR
10.34	1-Octene	Mineral oil
10.46	Cyclopentanone	Polyamide 6.6
13.15	Ethylbenzene	SBR
13.52	<i>o</i> -Xylene	SBR
14.27	1-Nonene	Mineral oil
14.50	Styrene	SBR
18.38	Phenol	Epoxy resin
18.80	$\alpha$ -Methylstyrene	SBR
19.05	1-Decene	Mineral oil
22.84	1-Undecene	Mineral oil
25.72	1-Dodecene	Mineral oil
27.98	1-Tridecene	Mineral oil
28.25	<i>p</i> -Isopropenylphenol	Epoxy resin
29.81	1-Tetradecene	Mineral oil
31.39	1-Pentadecene	Mineral oil
32.79	1-Hexadecene	Mineral oil
34.07	1-Heptadecene	Mineral oil
35.27	1-Octadecene	Mineral oil
36.44	1-Nonadecene	Mineral oil
37.59	1-Eicosene	Mineral oil

## CONCLUSION

Gas chromatography/mass spectrometry (GC/MS) and the analytical pyrolysis - gas chromatography/mass spectrometry has been proven as the valuable techniques for analysis and identification of mineral oils and polymeric materials in the failure analysis of materials used in the automotive industry. The identified materials could be then assigned to the corresponding car components. The obtained analytical results were used for troubleshooting with the customer and for remedial action of the technological process.

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