CDS Analytical

Analytical Solutions for the Automotive Industry

Analytical Solutions for Polymers & Coatings in the Automotive Industry

Modern polymers, including plastics and rubbers, hold the key to a host of safety and performance boosts in today's automotive industry. Plastics currently make up 50% of the volume of new cars but only 10% of the weight, which helps make cars lighter and more fuel efficient[1]. Novel plastic and rubber products also have improved passenger safety and auto designers rely on their versatility when designing new automobiles.

In addition to polymers, there has been improvement in paint technology. Although the newer paint styles may not have played a significant role in auto efficiency, recent paint innovations have kept cars looking newer longer as well as becoming more environmentally friendly when applied.

Complex solid materials, like black rubber, automobile paint, fibers and plastics, may be examined using a variety of techniques. Several of them include solvent extraction, headspace-GC/MS and FTIR but, they can present a real challenge to obtain a full analysis of the total chemical makeup. The use of GC/MS can provide a wealth of information about complex chemical systems, however the components usually must be volatile to be compatible with the technique.

Two "green analytical" techniques that can expand the use of any GCMS platform include pyrolysis and thermal desorption. Pyrolysis works by creating volatile compounds from seemingly incompatible materials like tires, vinyl plastics and carpet fibers. Precise heating of these samples at the GC inlet produces chromatograms, representing the various constituents of the sample, including additives, organic contaminants and the polymers. Each polymer breaks down at high temperatures (typically above 400C) and will provide a unique marker peak or pattern that can be used for identification.

Thermal Desorption can be utilized to concentrate volatile and semi-volatiles from air or a solid sample matrix. One major benefit is that they can increase the sensitivity of a standard GCMS by several orders of magnitude without the use of solvents or sample prep.

Also, heat can be applied (up to 350°C) on a solid sample which can be used to evolve and then trap semi-volatiles from large-solid samples.

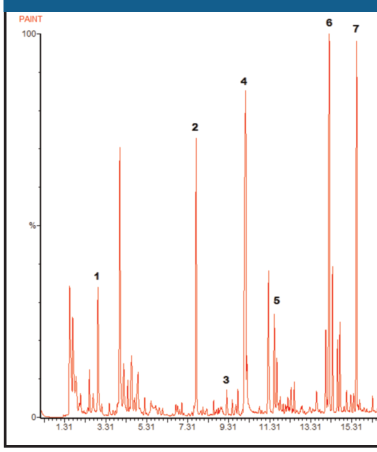
1.American Chemistry Council

The following examples represent several applications within the automotive industry and their suppliers, using both of these techniques. They can be commonly applied in the R&D lab, for QC as well as in meeting developed methods, such as VDA-278. In addition to the actual polymer identification, additives can be analyzed at low quantities including plasticizers, light stabilizers and antioxidants, among others.

Paint Analysis

Because it is so complex, comprised of many layers, and usually contains opaque fillers such as metal flake and titanium dioxide, automobile paint is a very challenging analytical sample. Each layer is formulated for specific properties, and may include acrylics, epoxies, urethanes and other polymer systems. Pyrolysis delivers the organic content to the GC/MS and leaves the inorganics behind, simplifying sample preparation.

Figure 1: Automobile Paint, Whole



1. Butanol
2. Methyl methacrylate
3. Butyl acrylate
4. Butyl methacrylate
5. Hydroxypropyl methacrylate
6. Octyl methacrylate
7. 5-isocyanato-1-(isocyanatomethyl) -1, 3, 3-trymethyl cyclohexane

Some analysts will prepare a sample of the entire paint, producing a complex pyrogram of the whole system, while others prefer to re-move the paint layer by layer and look at each one individually. Figure 1 shows the pyrogram made from a whole paint, and-contains peaks for several acrylics, plus a diisocyanate generated from a polyurethane. Figure 2 shows just a clearcoat, which also contains a variety of acrylic monomers, plus styrene. The 2-ethyl hexanol is probably a degradation product from the 2-ethylhexyl acrylate, and is sometimes seen in systems using DOP as a plasticizer.

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Figure 2: Automobile Paint, Topcoat

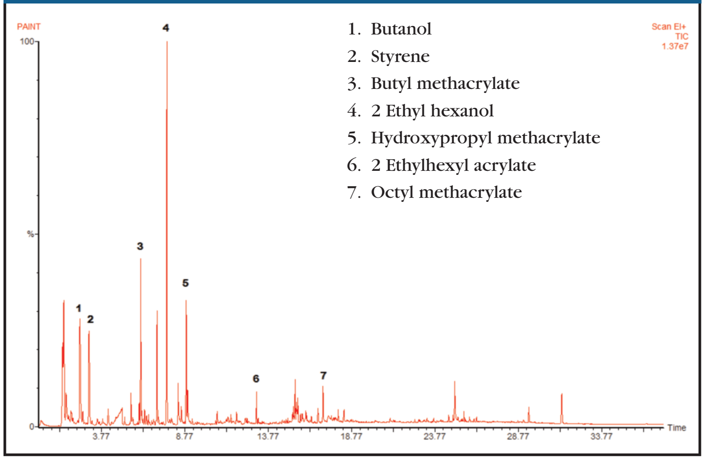
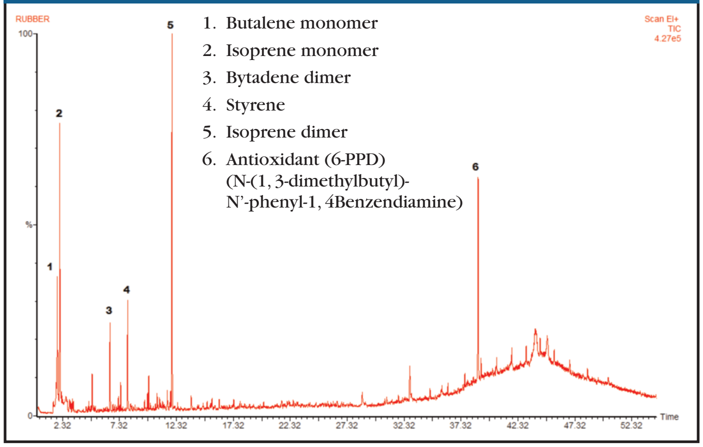


Figure 3: Synthetic Tire Rubber

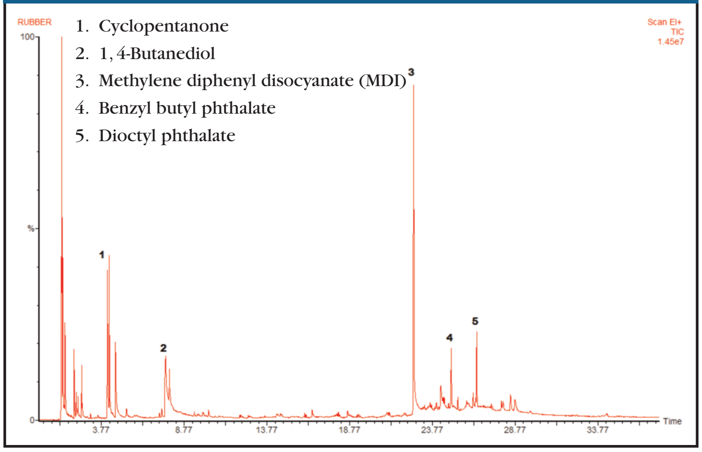


Rubber

The polymers used for rubbers, both natural and synthetic, are easily differentiated and analyzed using Py-GC/MS. In general, these polymers degrade to produce some monomer, so the type of rubber is readily determined. In the case of natural rubber (polyisoprene) the two largest peaks are for the monomer and the dimer of isoprene. Figure 3 shows the analysis of a synthetic automobile tire rubber formulated from butadiene, isoprene and styrene, with an antioxidant (6PPD) added. Peaks are produced for each of the monomers used, and may provide quantitative information about the relative amounts of each.

Figure 4 shows a polyurethane rubber, different from the polyolefins. Nevertheless, it is easily identified as a polyurethane by the presence of the diisocyanate used. The polyol involved is a polyester type, using adipic acid, which produced the cyclopentanone peak. In this case, two different phthaltes are used as plasticizers.

Figure 4: Polyurethane Rubber



Carpet Fibers

Fiber blends are like other polymer blends or mixtures when analyzed by Py-GC/MS in that the individual polymers pyrolyze independently, and the resulting pyrogram contains pyrolysates from each of the constituents. Figure 5 illustrates this process for a blend of Polyethylene terephthalate (PET) and Polyacrylonitrile (PAN). The top pyrogram in Figure 5 is PET only, showing the typical pyrolysis products, including benzoic acid, listed in Table 1. The bottom pyrogram is for PAN only, and has large peaks for acrylonitrile monomer and dimer. The blended fiber is in the middle, and has the characteristic peaks of both the individual fibers. Since the pyrolysis products of each polymer rarely interact with each other, comparing the amount of a product generated from one fiber to a compound from the other can be used

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Figure 5: PAN/PET Fiber Blends

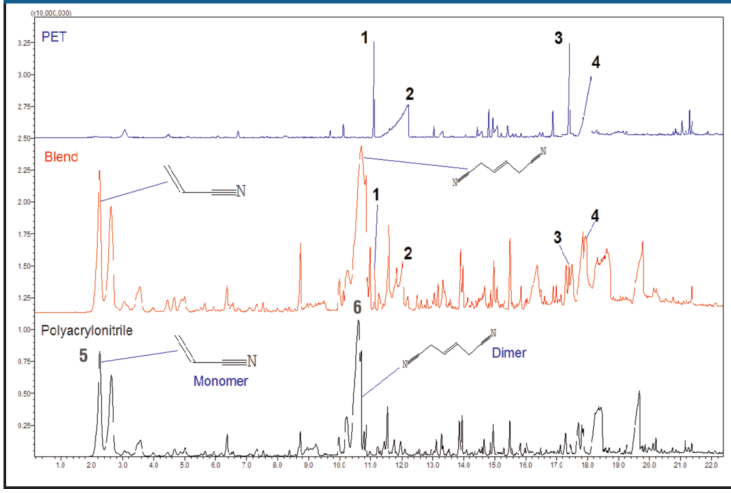


Table 1:

1. Vinyl benzoate
2. Benzoic acid
3. Divinyl terephthalate
4. Terephthalic acid monovinyl ester
5. Acrylonitrile
6. Hexene dinitrile

Published Papers and Application Notes

Published Papers

Automotive Paint Analysis using Pyrolysis-GC-TOFMS and Pyrolysis-GCxGC-TOFMS

LECO Corporation, St. Joseph, MI.

NHTSA Tire Aging Study using Pyrolysis GC-MS

Uday Karmarkar, Ana Barbur, Edward R. Terrill, Mark Centea, Larry R. Evans, James D. MacIsaac, Jr.

Akron Rubber Development Laboratory, Inc., Akron, OH

U.S. Dept. of Transportation Research Center, National Highway Traffic Safety Administration, Washington, DC

A Simple Polymer Identification Scheme

Paint & Coatings Industry Magazine

Thomas Wampler, Charles Zawodny, Karen Jansson, CDS Analytical, Oxford, PA

Recent Changes in Automotive Paint Formulation using Pyrolysis-Gas Chromatography/Mass Spectrometry for Identification

Journal of Analytical and Applied Pyrolysis

Gregory A. Bishea, FBI, Washington, DC

William J. Simonsick, E. I. DuPont de Nemours and Co., Philadelphia, PA

Thomas P. Wampler, CDS Analytical, Inc.

Analysis of Rubber Materials by Pyrolysis GC

Rubber World

Maxine Phair, Thomas Wampler, CDS Analytical, Inc.

Polymer Additive Analysis using Multi-Step Thermal Sampling-GC/MS

LabPlus International

Thomas Wampler, CDS Analytical, Inc.

Multi-Step Thermal Characterization of Polymers Using GC/MS

T. P. Wampler, C. P. Zawodny, K. D. Jansson, CDS Analytical, Inc.

CDS Application Notes:

Pyrolysis-GC/MS of Polyurethanes

CDS Analytical App Note #71

Pyrolysis of Rubber with Antioxidant 6-PPD

CDS Analytical App Note #80

Analysis of a Layered Paint Sample using Pyrotomy

CDS Analytical App Note # 90

VDA 278 Analysis using Thermal Desorption with a GC/MS System

CDS Analytical App Note #97

Using a Thermal Technique to Extract Residual Oligomers

CDS Analytical App Note #110

Identifying Additives in a Pyrogram using Deconvolution Software

CDS Analytical App Note #113

Pyrolysis of the Bisphenol A Polymers Epoxy and Polycarbonate

CDS Analytical App Note #160

Pyrolysis-GC/MS in the Analysis of Fiber Blends

CDS Analytical App Note #162

Pyrolysis of Fluoropolymers Polyvinyl Fluoride vs. Polyvinylidine Fluoride

CDS Analytical App Note #164

CDS Users

ACH-Glass Systems, MI
AGC Automotive Americas, MI
Akron Rubber Development Laboratory Inc., OH
AKZO Nobel Coatings Inc. MI
AKZO Nobel Ltda. Sao Paulo
Autoneum MI
Bodycote Testing Group - EXOVA, MI
Bridgestone Americas CRT, OH
Brisa Bridgestone, Turkey
Chrysler Group LLC, MI
Continental Structural Plastic, MI
Delphi Packard, OH
DuPont Performance Coatings LLC, DE
DuPont Textiles & Interiors Inc., VA
Esmalglass S.A.U., Castellon
FAW - Volkswagen, China
Federal Mogul Corporation North America, KY
Federal Mogul Powertrain, MI
Ford Motor Company, MI
Freudenberg-NOK Sealing Technologies, MI
Gates Corporation - AAG, MI
GE Plastics, AL
Gebauer & Griller Kabelwerke GesmbH, Austria
General Motors, MI
Gentex Corporation, MI
Goodyear Tire & Rubber Co., OH
Haartz Corp., MA
Honda of America Mfg., Inc., OH
Illinois Toolworks Technical Center, IL
International Automotive Components, NA, MI
JK Tyre & Industries Ltd., India
Lucite International, Inc., TN
Magna E-car Systems, MI
Malaysia Rubber Board, Malaysia
Meritor, MI
Michelin North America, SC
Navistar, IL
Omnova Solutions, OH
Omnova Solutions, SC
Owens-Brockway Glass Container Inc., OH
Parker Seal, KY
Phelps Dodge Magnet Wire Co., IN
Pilkington North America Inc., OH
Plaskolite West Inc., CA
Plastipak Packaging Inc., IL
PPG Coatings Innovation Center, PA
PPG Industries Inc., Australia
PSA Peugeot Citroen, France
PT Gajah Tunggal Radial, Indonesia
RenaultFrance
Robert Bosch Corp., SC
Siegel Robert Automotive, TN
Takata, MI
Teknor Apex Co., RI
The Carlstar Group, MO
Toray Industries, Inc., Tokyo
Valeo, France
Valspar, MN
Valspar Corporation, PA
Valspar Corporation Ltda., Brazil

to determine the relative amounts of each of the polymers present.

Newer carpets are now being manufactured with biopolymers, making them environmentally friendly, with up to 30% or more of renewable materials. Biopolymers give totally different responses then traditional industrial polymers and identification, and quantitation, of each polymer in the blend is straight forward.

VDA 278

VDA 278 is the thermal desorption analysis for organic emissions from interior components of a vehicle. This analysis deals with a VOC value, or the new car smell, (up to C20-Eicosane) based on Toluene, and a FOG value (C16-C32) based on C16 (Hexadecane). In general, the method demonstrates the emissions coming from non-metallic molded parts occurring in motor vehicles. Materials such as textiles, adhesives, foam, leather, and similar substances are included. This method is used for both qualitative, as well as, semi-quantitative evaluation of the degassed emissions. The VOC emissions are reported semi-quantitatively as toluene, whereas the FOG value is reported as condensable substances found in the materials as hexadecane. Single substances of the emission can also be identified and quantitated using this method or a variation of this method.

The example below shows a serial dilution made of a Kovats VOC standard (100µg/ml) to give a final concentration of 10ng/µl in CS2. A thermal desorption tube (6") packed with Tenax was spiked with the standard VOC mix (20ng/2µl). The tube was thermally desorbed for 280°C/30min interfaced to a GC/MS.

The GC parameters were established to resolve C8 (octane) to C20 (Eicosane) and C8 to C 27 (for FOG analysis). A corresponding analysis of carpet fibers was performed by placing them into an empty 6" desorption tube and desorbing them for 30 minutes at 90°C for the VOC value (Figure 6) and for 60 minutes at 120°C for the FOG value (Figure 7). A number of aliphatic hydrocarbons were identified (C14,C15,and C16) in the VOC portion as well as a propanoate ester and a number of long chain alkyl benzenes. The FOG fraction had a number of aromatics, phenol, benzyl alcohol, as well as, caprolactam. There were also long chain aliphatic alcohols and several alkanes detected.

Molded Plastics

From bumper to bumper, plastics are used externally and internally as well as for high temperature engine applications, the electrical system and powertrain. The diversity of polymers and additives needed for these applications is extensive.

When analyzing plastics, whether for R&D or QC, it is more then just about the polymers themselves. There are also the additives and possible organic contaminates that play a role for the selected application and for quality.

There are several analytical techniques that can be used to analyze for individual components in a polymeric sample including FTIR, solvent extraction-GCMS, TGA-MS, HPLC, among others. However, these techniques do not normally lend themselves to analyze for the complete polymeric system, which includes volatile and semi-volatiles, as well as the actual polymer. But using a pyrolyzer as a "thermal extracting system"

Figure 6: VOC Value Runs

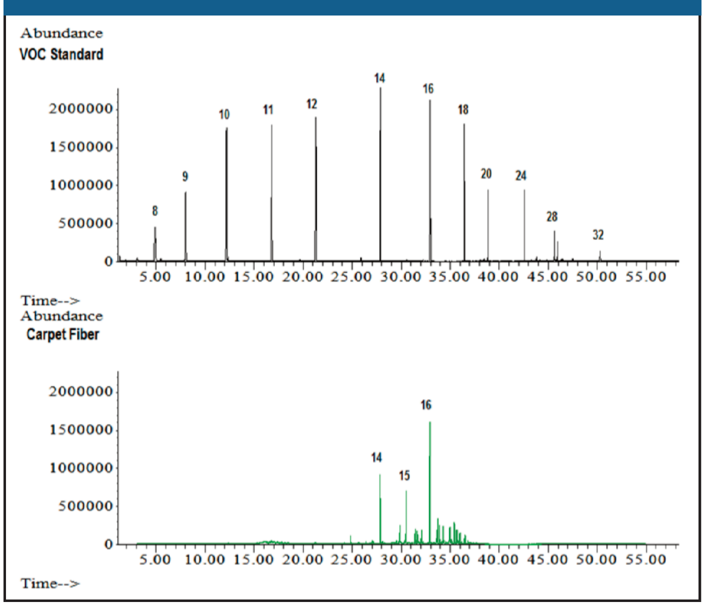


Figure 7: FOG Value Runs

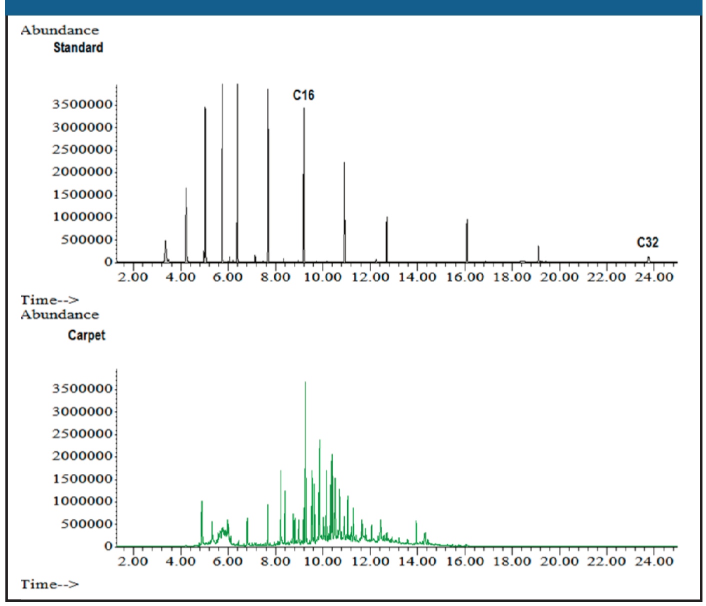
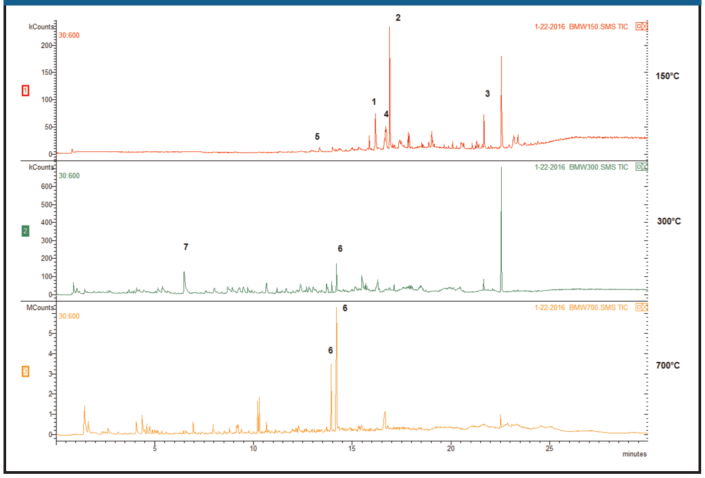


Figure 8: 3-Step Run of Auto Dashboard



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in combination with a GCMS, provides a simple and direct means of analyzing not only the additives, but the polymer itself. By careful selection of the sampling temperature, volatile and semi-volatile compounds may be liberated from the polymer matrix for analysis without the use of solvents or complex sample preparation. The remaining sample may then be pyrolyzed to identify the type and even the structure of the polymer. A typical series of analyses includes a low temperature assessment to identify volatiles such as solvents and retained monomer. An intermediate temperature is used to investigate semi-volatiles like antioxidants, plasticizers and lubricants. Finally, at pyrolysis temperatures, the polymer itself may be identified.

The following example is from the dash board of a late model European sedan. Figure 8 shows a three-step run programmed at 150C, 300C and then 700C, which is designed to analyze for the additives as well as the polymers.

Peaks one and two, n-hexyl salicylate and homosalate respectively, are actually from a cleaning/protectant spray put onto the dash board. The first is a fragrance compound and the second is a UV stabilizer. Peaks 3 (Bis 2-ethyl hexyl phthalate) and peak 4 (Di isobutyl phthalate) are plasticizers. One other additive found in the first run was an anti-oxidant, 2,4 di tert-butyl phenol (peak 5).

Looking at the run at 300C, we can see the polymer starting to break down and from peak 6 (Isophorone diisocyanate or IPDI), we can determine that the polymer is a polyurethane. And from some of the other fragments, such as 5-acetyloxy, 2-pentanone (peak 7), it is an ester-based polyurethane.

Lastly, looking at the final run at 700C, the polymer fully degrades and we can see both isomers of IPDI, which we would expect from a polyurethane made from this structure.

Instrumentation

CDS Analytical has a long history of working with the automotive industry. We have several models of pyrolyzers and thermal desorbers that can be applied to meet the organic analysis needs in both, the R&D and QC lab. But one particular favorite has been our Model 5200. This instrument is unique in that it can be used for polymer analysis, including the additives, as well as operating as a traditional thermal desorber to meet the needs of VDA 278. Connection can be made to most GC/MS instruments and you can easily share your existing GC/MS with your other injection devices.

CDS also has polymer and additive libraries which can aid the user in identification of unknowns. These libraries can play an important role when you are deformulating an unknown sample matrix. If you are interested in learning more or would like us to provide a sample analysis to help prove out an application, we would look forward to hearing from you.

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