Analysis of Automobile Paints Using Pyrolysis-GC/MS

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Introduction

Automotive finishes are highly complex polymer systems made of multiple layers of copolymers, each formulated to perform a specific function. In addition to the various organic materials used in the paint, the inclusion of inorganic compounds such as metal oxides and aluminum particles for opacity and visual effect make the finished product difficult to analyze using standard laboratory instruments. They may, however, be analyzed by gas chromatography mass spectrometry (GC/MS) with the addition of a pyrolyzer (Py) at the GC inlet. Pyrolysis reduces the polymeric content of the paint to volatiles compatible with gas chromatography and mass spectrometry, leaving the inorganic constituents behind. Consequently, Py-GC/MS has become the method of choice for forensic laboratories analyzing paint fragments[1] in criminal investigations, as well as for paint analysis by manufacturers for quality control and product deformulation.

In this Field Application Report, two automobile paints are compared using Py-GC/MS. The analytical system consisted of a PerkinElmer® Clarus® 500 GC/MS interfaced with a CDS Analytical Pyroprobe 2500 Pyrolysis Autosampler*. Using this integrated system, samples are rapidly pyrolyzed, automatically introduced into the GC carrier stream and transferred to the GC column for analysis.

The paints used for automobiles usually include familiar polymer monomers such as methyl methacrylate, styrene, butyl acrylate and butyl methacrylate. In addition, chromatographic peaks are also observed for compounds used to provide cross-linking, plasticity, durability and other functionalities.

Experimental

Table 1 (Page 2) lists the analytical parameters used for these analyses. The paint fragment sample is introduced as a solid in a quartz tube, so no solvent peak is generated and all peaks in the chromatogram are the result of constituents of the sample material. Typical samples are approximately 10-100 µg, taking into account both the trace amount of the evidence material and the capacity of the GC column and mass spectrometer. Sample preparation consists of placing the paint sample into the quartz tube, which is introduced from a carousel into the pyrolysis coil of the pyrolyzer. An on-line/off-line valve permits venting of air from the system before it is connected in-line to the GC, equilibration with the GC carrier before the run is started and removal of the sample after pyrolysis.

* Available for purchase directly from CDS Analytical Inc., 1-800-541-6593, www.cdsanalytical.com

Results

The total ion chromatogram produced by Py-GC/MS (the pyrogram) of a typical automobile paint is shown in Figure 1. This paint is formulated using many common monomers, such as styrene and butyl methacrylate, which are easily identified through library searching of their mass spectra. Figure 2 shows the mass spectrum of the peak labeled number 7, which is identified as hydroxypropyl methacrylate. Hydroxy methacrylates are added to the paint to provide a cross-linking site which is used during the curing process. Eight of the peaks in this pyrogram are identified in Table 2.

Because these paints are fairly complex and generate many chromatographic peaks when pyrolyzed, different paints may be distinguished by a comparison of their pyrograms. Different automotive finishes may contain the same monomers but in different relative amounts, or one may contain a monomer or constituent not found in the other. Figure 3 shows the pyrogram of a second automobile paint for comparison to the first. These paints differ in both the relative amounts of the monomers that they have in common and the presence of compounds in one pyrogram not seen in the other.

In Figure 4, the first 13 minutes of the two pyrograms for both paint samples have been expanded for easier comparison. The previously identified components from Paint 1, including common monomers, are also labeled on Paint 2, where present. Although each paint contains methyl methacrylate, styrene and butyl acrylate, the relative amounts of these, especially the styrene and butyl acrylate, are substantially different.

Identification of the specific monomers and other constituents used in a paint formulation does more than just make it possible to distinguish one paint from another.

Table 1. Instrument Parameters.

Clarus 500 GC		**Clarus 500 MS**	
Injector Temperature:	300 ˚C	Mass Range:	30-550 u
Oven Program:	40 ˚C for 2 min	Scan Time:	0.39 sec
Rate:	8 ˚C/min	InterScan Delay:	0.01 sec
	295 ˚C for 10 min	Transfer Line:	250 ˚C
Column:	Elite-5MS* 30 m,	Solvent Delay Time:	0 sec
	0.25 mm I.D., 1.0 µm film	Source Temperature:	280 ˚C
Carrier Gas:	He (split ratio 50:1)	Multiplier Voltage:	350 V
		Trap Emission:	100 µA
Model 2500 Pyrolyzer			
Oven:	300 ˚C		
Transfer Line:	300 ˚C		
Pyrolysis Temperature:	750 ˚C		
Pyrolysis Time:	15 sec		
Heating Rate:	10 ˚C/ms		

* PerkinElmer part number N9316283

Table 2. Peak Identifications.

Peak Number	Compound
1	Methyl Methacrylate
2	Methacrylic Acid
3	Styrene
4	Butyl Acrylate
5	Butyl Methacrylate
6	Hydroxyethyl Methacrylate
7	Hydroxypropyl Methacrylate
8	Octyl Methacrylate

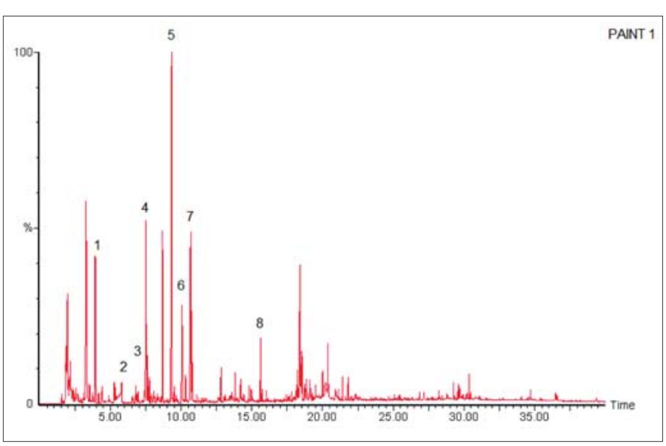

Figure 1. Total Ion Chromatogram resulting from the pyrolysis of a paint sample at 750 ˚C for 15 seconds.

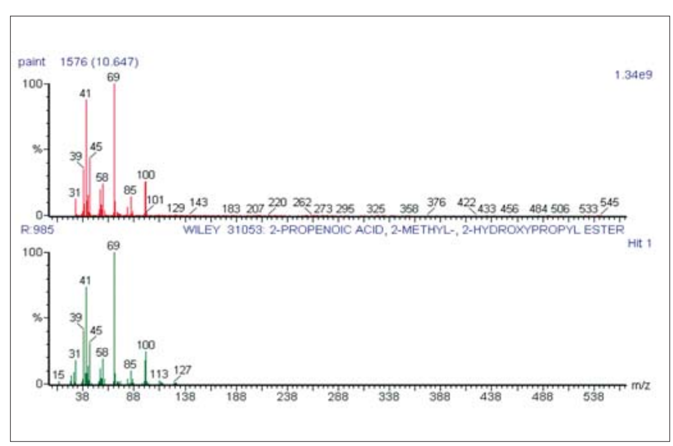

Figure 2. Mass spectrum of peak number 7 from the pyrogram shown in Figure 1, identified as hydroxypropyl methacrylate.

Since automobile paints have changed substantially over the years[2], Py-GC/MS also helps to establish the approximate age of the car involved. Very early in automobile production, most paints were glyceryl phthalate polyesters, which look considerably different from the modern acrylics. Later, paints were favored which were primarily poly methyl methacrylate. The addition of high concentrations of cross-linkers permits the use of paints with a higher solids load relative to the solvent and reduces emission, a more recent development. All of these changes make it possible to create libraries of paint programs, which help identify the type of car involved in a forensic investigation.

Since other types of paints are formulated with the same kinds of monomers, the same analytical techniques may be used in the study of a wide variety of paints, varnishes and coatings for the purpose of identification, quality control, museum conservation work, competitive product deformulation and performance studies.

Conclusions

Automotive finishes are polymeric systems incorporating a wide variety of monomers which give them specific characteristics. Analytical pyrolysis largely unzips these polymers to produce chromatograms containing peaks for the various monomers used. The presence or absence of specific monomers helps distinguish one paint from others, as does the relative amounts of the monomers common to two paints. It also helps to determine the approximate age of the paint. The presence of inorganic materials in the paint does not interfere with this process – the polymers are simply pyrolyzed to volatiles, leaving the inorganic constituents behind.

Although the identification of automobile paints from the small samples needed for GC/MS is extremely valuable to forensic laboratories, the same techniques can be applied in other labs as well. Quality control, product age, authenticity and performance concerns are addressed in industry and museum laboratories routinely using pyrolysis-GC/MS.

References

1. J.M. Challinor, Pyrolysis Techniques for the Characterization and Discrimination of Paint, in Forensic Examination of Glass and Paint, B.Caddy (Ed.) Taylor & Francis (2001).

2. T.P. Wampler, G.A. Bishea and W.J. Simonsick, Recent Changes in Automotive Paint Formulations using Pyrolysis-Gas Chromatography/Mass Spectrometry for Identification, J. Anal. Appl. Pyrolysis, 40-41 (1997) 79-89.

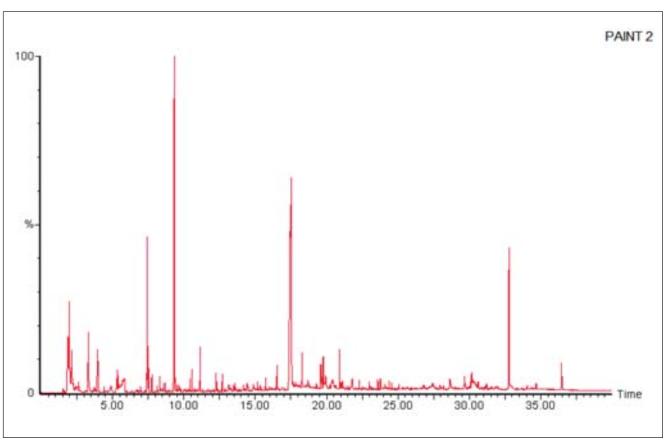

Figure 3. Pyrogram of an automobile paint using a different formulation.

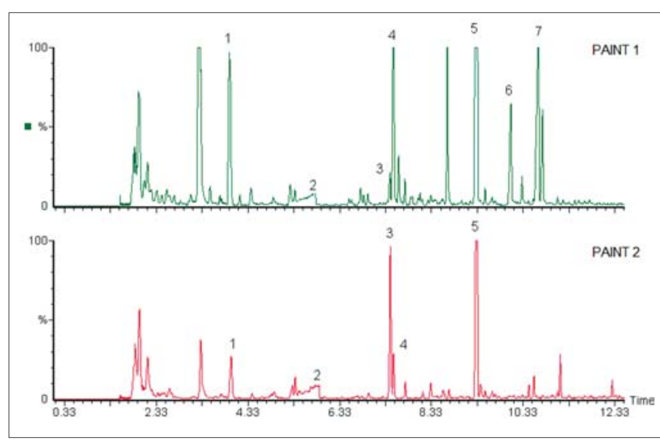

Figure 4. Expansion of the monomer region of the pyrograms for the two different paints. Peak identifications are listed in Table 2.

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