Gas Chromatography in Coatings Analysis

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Gas chromatography (GC) is an established standard analytical tool for the analysis of coatings and related materials. Many volatiles and semivolatile compounds such as residual monomers, solvents, and plasticizers, and low molecular weight additives such as mildewcides and antifoaming agents can easily be analyzed by GC. Headspace–gas chromatography/mass spectrometry (HSGC/MS) is used for routine analysis of odor problems and for analyzing volatiles in situations where solvent extraction and/or sample dilution are not appropriate. Less volatile compounds, such as polymers, resins, and waxes can be analyzed by pyrolysis/GC-MS and/or derivative pyrolysis-GC/MS, such as methylation with tetramethylammonium hydroxide (TMAH).

INTRODUCTION

Gas chromatography (GC) continues to play a vital role in the analysis of coatings and related materials. This article focuses primarily on those areas where new insights have emerged in the literature and in our laboratories in the last several years. The reader is encouraged to review references 1–4. Gas chromatography involves a sample being vaporized and injected onto the head of the chromatographic column. A schematic diagram of the basic components in a GC system is shown in *Figure* 1. The sample is transported through the column by the flow of inert, gaseous mobile phase (Ar, He, CO_2, and N_2). The choice of a carrier gas normally depends on the type of detector used. The column itself contains a liquid stationary phase, which is adsorbed onto the surface of an inert solid.

Column Packing Material

The column packing material must be capable of withstanding high temperatures (up to 350°C) and moderate pressures (up to 5 atm), and they should be inert and available in different particle sizes. Other important physical parameters include particle size (smaller particle sizes provide more plates), porosity and surface area (a larger surface area which is determined by porosity will require more liquid phase to achieve a complete coating), and the packing density. Some

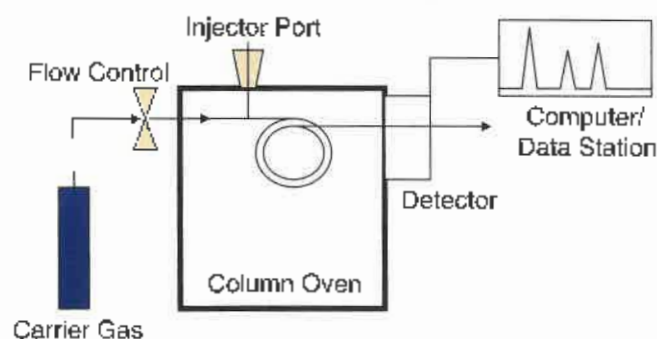Figure 1—Schematic diagram of the basic components in a GC system.

Table 1—Commonly Used Columns

Stationary Phase	Temperature Range	Applications
100% Methyl polysiloxane	–60°C to 350°C	General purposes, e.g., hydrocarbons, amines, solvents, waxes, phenols
Polyethylene glycol	60°C to 225°C	Amines, acids, alcohols
50% Phenyl-50% methyl polysiloxane (e.g., DB5)	–60°C to 350°C	Alcohols, acetates, phenols, drugs, sugars, pesticides, and herbicides

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Analytical Series

examples of solid packing materials include Chromosorb P, which is sourced from firebrick, and Chromosorb W, which is sourced from Celite Filter Aid. Each of these packing materials may be treated with a silylating reagent like dichlorodimethyl silane (DMDCS) to cover the active silanol functionalities on the surface, or may be treated with acid or base to remove active metal contamination. Some examples of commonly used columns are described in *Table* 1.

Detectors Used in GC

Thermal conductivity detectors (TCD) and flame-ionization detectors (FID) are excellent detectors for routine types of analysis, for example, in Quality Control (QC), because they provide retention times which are very reproducible and are compound specific (retention times), when the analyses are done under the same GC conditions. The only drawback of these detectors is that they are not very specific. GC has very low detection limits, which is advantageous for quantitative analysis of monomers. Mass spectrometers (MS) are the detectors of choice when one is interested in detailed information for unknown analytes which cannot be identified accurately by retention times alone.

The compounds can be identified by their retention times and/or the relative abundances of various charged fragments, as shown in *Figure* 3.

PYROLYSIS-GC/MS

Pyrolysis-GC/MS remains the major area of GC application in coatings. Its strength is its ability to analyze nonvolatile organic samples, such as resins and polymers. Here, the GC is fitted with a pyrolysis unit, which is interfaced to a GC/MSD system (*Figure* 4). Such an arrangement provides valuable information on a coating, ranging

Figure 2—Chromatogram of a mixture of various monomers and solvents obtained by using a capillary column (DB5, 30 m ˊ 0.25 mm ˊ 0.25 mm) in a GC/MS system. The chromatogram shows clearly well-resolved peaks in a mixture of monomers and solvents.
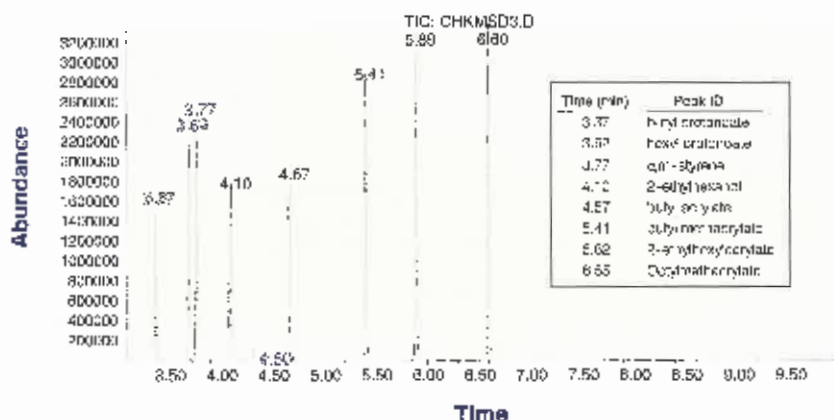
Figure 3—Mass spectral fragments of the peak eluting at 3.77 min in *Figure* 2 with the corresponding library match identifying it as a, m-styrene.
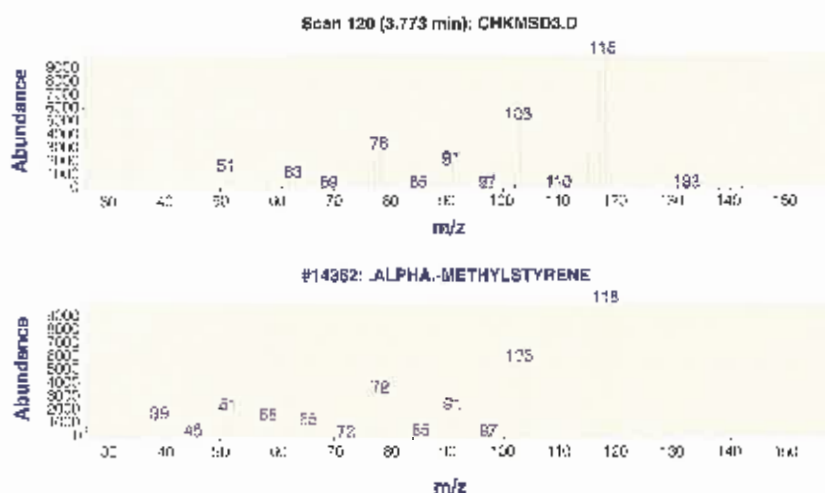
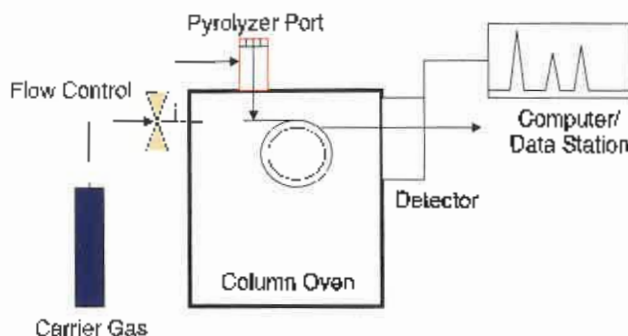Figure 4—Schematic diagram of a pyrolysis-gas chromatograph system.

Figure 5—Pyrogram of an acrylic copolymer based paint. The main monomers are methyl methacrylate (MMA) and butyl acrylate (BA).
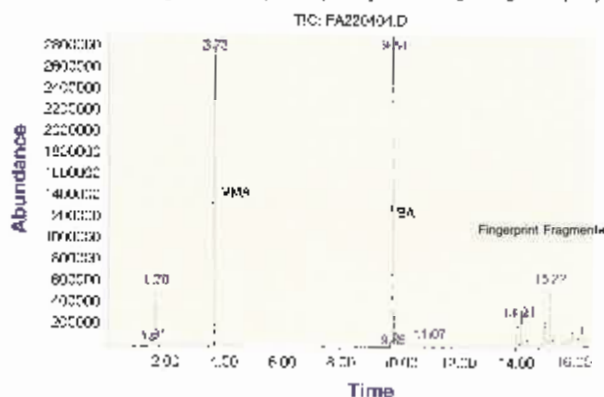

Figure 6—Mass spectral fragments of the peak eluting at 3.75 min in *Figure* 5 with the corresponding library match identifying it as methyl methacrylate (MMA).
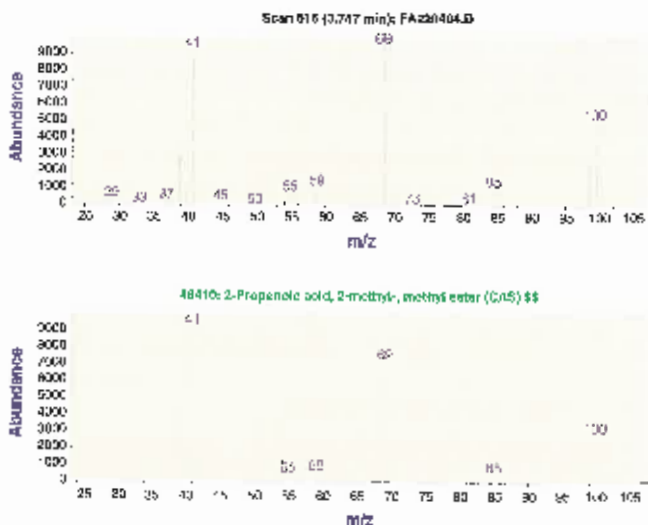

Figure 7—Mass spectral fragments of the peak eluting at 9.76 min in *Figure* 5 with the corresponding library match identifying it as styrene. It is possible that styrene could be a seed polymer or a low level contaminant.
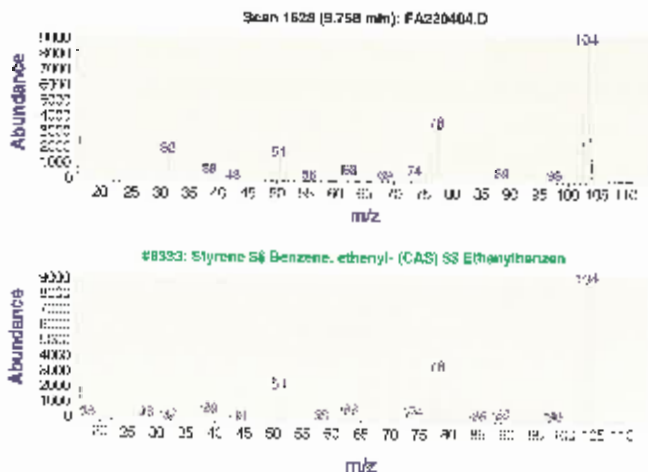

Figure 8—Mass spectral fragments of the peak eluting at 9.84 min in *Figure* 5 with the corresponding library match identifying it as butyl acrylate.
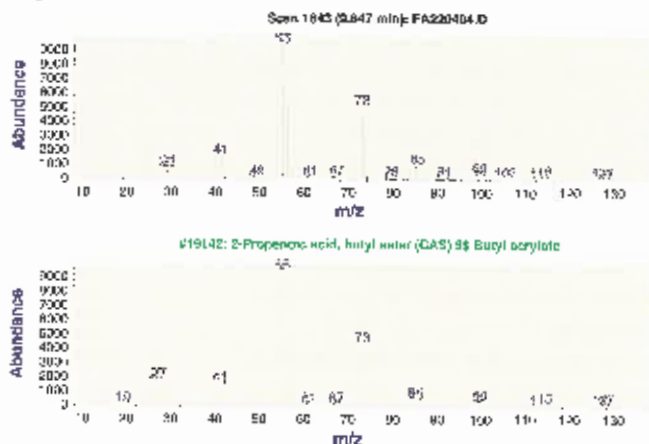

Figure 9—Gas chromatogram of residual monomers in an emulsion. The peaks are identified by both retention time and mass number.
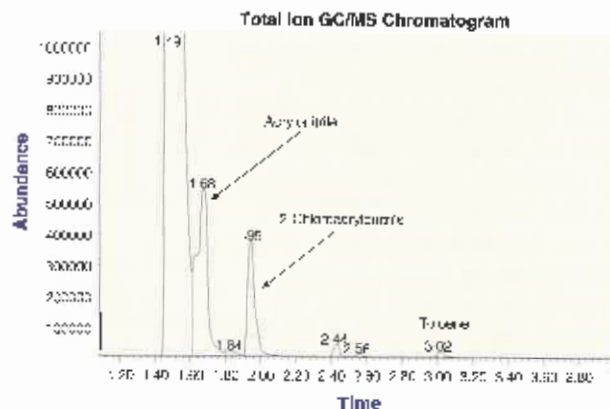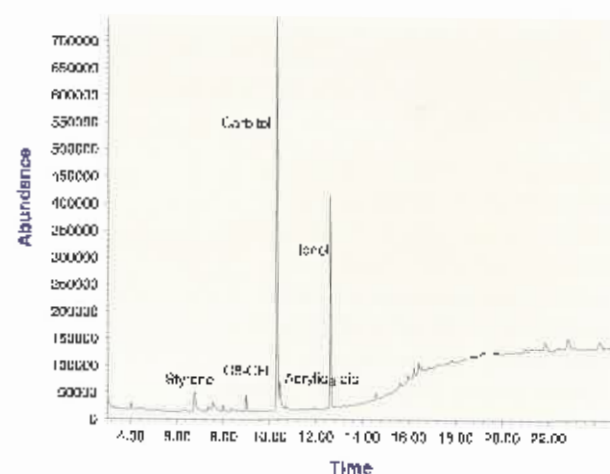

Figure 10—Gas chromatogram of solvents, coalescent, and residual monomers in an emulsion.

from solvent, plasticizers, and other additives to the determination of the polymer composition. For this method to work, the polymer must be unzipped by fast heating to temperatures greater than 400°C in an inert atmosphere. This procedure reduces the high molecular weight polymer to fragments amenable to GC analysis. Normally, the low molecular weight fragments are characteristic of the starting polymer. For example, acrylics generate large amounts of the original monomers. Typically, wet or dry samples can be analyzed either by ribbon or coil probes. The material is pyrolyzed instantly at 700–800°C for 10–20 sec. Normal pyrolysis runs are between 30–40 min. However, with high-speed GC systems, analysis time can be as short as 60–120 sec. Short analysis times are achieved with short narrow columns or high flow rates, high temperature oven ramps, and high speed detectors for high-speed separations.

Alternatively, the reduction of higher molecular weight condensation polymers to low molecular weight fractions amenable to GC analysis can be achieved via chemical degradation reactions. The low molecular weight species generated in this fashion are normally related to the starting polymer.

Normally, the pyrograms are complex but can serve a variety of purposes, ranging from additives identification to providing compositional fingerprints, which can be matched to controls. Good understanding of the thermal degradation/pyrolysis mechanism is very important for proper interpretation of the results. There are three degradation paths depending on the polymer type: (1) unzipping; (2) random chain fragmentation; and (3) non-chain scission.[5]

The peaks labeled "fingerprint fragments" in *Figure* 5 are also very important in polymer analysis. They can be used in product quality control analyses. Numerous practical examples of typical pyrolysis-GC and derivative pyrolysis-GC of polymers have been published by Levy and Wampler,[6] and Washall and Wampler.[7]

HEADSPACE–GC

Typically, a sample of interest is heated in a sealed container at a given temperature and time (for example, 150°C for 30 min). Then a sample of the volatiles in the sealed container (gas) is introduced into a GC system with the carrier gas. Commercially assembled systems of this kind are called Headspace analyzers.

Representative GC Application Areas

RESIDUAL MONOMERS: The residual monomer level in commercial latexes typically does not exceed 1000 ppm and in many cases is below 100 ppm. Headspace GC or straight GC is an excellent method for determining the

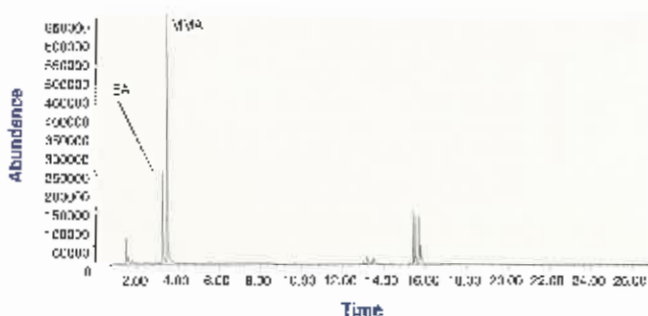Figure 11—Pyro-GC/MS chromatogram of a control EA/MMA paint system.

Figure 12—Pyro-GC/MS chromatogram of a EA/MMA paint system that had failed.
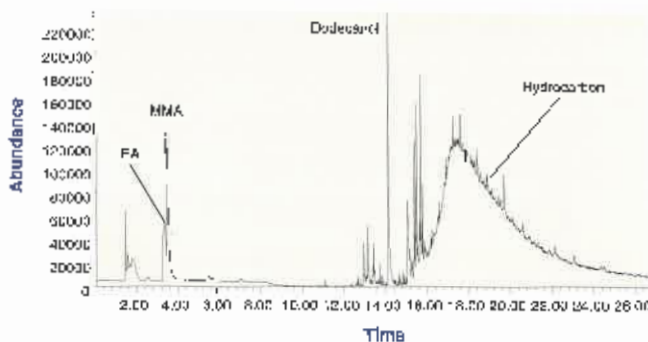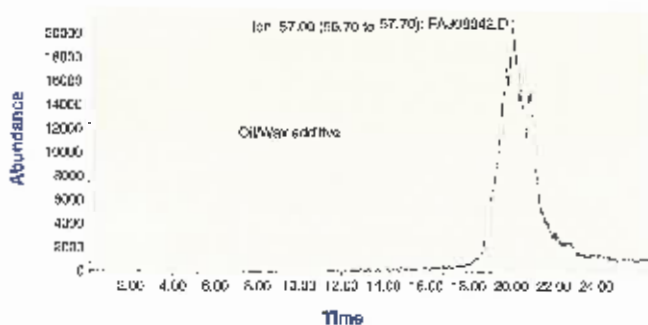

Figure 13—Pyrolysis-GC of THF extract of a paint that had an oil/wax additive. The selected ion mass (m/e = 57) spectral data indicate hydrocarbons with carbon lengths ranging from C_{18}-C_{45} (*Figures* 12 and 13).

types and levels of residual monomers. In a typical GC analysis, between 5–10% of an emulsion is prepared and centrifuged to extract the residual monomers and the supernatant is injected into the GC. The detection limit of monomers in emulsions is around 10 ppm.

SOLVENTS, COALESCENT, AND PLASTICIZERS: Nearly all latex polymers paint formulations with a minimum film formation temperature (MFT) of 5°C must contain a low volatility solvent to act as a temporary plasticizer to enhance polymer interdiffusion, which aids in film formation. These solvents may or may not be water solu-

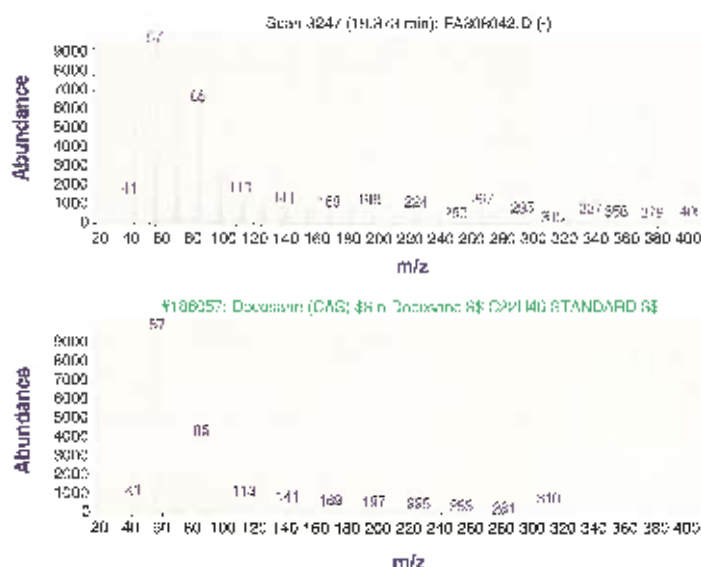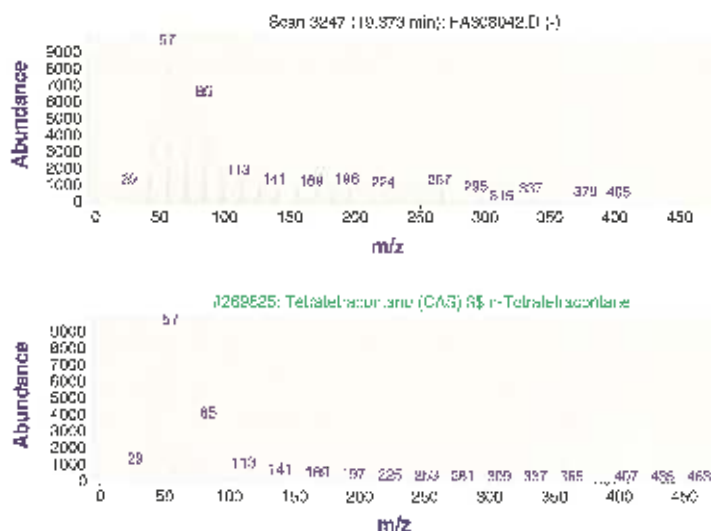Figure 14—Mass spectral data in *Figure* 13 is consistent with n-docosane.

Scan 3247 (19.3?4 min): FA306042.D (-)

#188057: Docosane (CAS) $$ n-Docosane $$ C22 H46 STANDARD $$

Figure 15—Mass spectral data in *Figure* 13 is consistent with tetratetracontane.

Scan 3247 (19.373 min): FA308042.D (-)

#269525: Tetratetracontane (CAS) $$ n-Tetratetracontane

ble, e.g., diethylene glycol butyl ether is water-soluble while Texanol (3-hydroxy-2,2,4-trimethylpentyl isobutyrate) ester alcohol is not. In a typical analysis, about 2% THF/paint mix is centrifuged to insoluble polymer and pigments. The supernatant is then injected into the GC for analysis.

Alternatively, a known amount of the paint or emulsion is put in a headspace vial, sealed and heated to 130°C for 5–10 min and the gas injected into the GC/MS for analysis.

ASTM methods for the analysis of paints using gas chromatography include: D 1983 and D 2800 for fatty acids, D 2245 for the identification of oils and oil acids, D 3960 for VOCs in paints, D 3009 for spirits, and D 3271 for solvents.[b]

COATING FAILURES: GC, pyrolysis-GC/MS, and headspace GC can be used effectively to solve coating fail-

ure problems. For example, if coating failure is due to the use of a wrong (different) batch of paint, one can look at the solvent composition by GC or, by headspace GC one can look at the solvent composition by GC or, in cases where only the dry paint is available, by headspace GC. By comparing fingerprint data of the residual solvent of the failed paint to the control, one can easily identify whether a sample has been adulterated.[9]

It can be concluded from *Figures* 11 and 12 that the coating failure is most likely due to the presence of contamination, which has been identified as long-chain hydrocarbons and dodecanol.

LOW-LEVEL ADDITIVES AND WAXES: Pyrolysis-GC is also suitable for analyzing low-level additives, which are less volatile due to their relatively high boiling points, for example, waxes and oils. *Figure* 13 shows a pyrogram of a sample containing low levels of a high boiling point hydrocarbon ranging from about C_{16} to C_{46} wax/oil. A selective m/e = 57 extraction reveals an ion fragmentation pattern which is consistent with wax/oil components, such as docosane and tetradocosane (*Figures* 14 and 15).

Other Areas of Application

Additional applications include analysis of condensation polymer systems,[2] alkyd and polyester resins, silicone polyesters, polyurethanes, epoxy resins, polysiloxanes, polyamides, vinyl polyesters, phenol formaldehyde resins, rosin derivatives, and cellulosics derivatives.

CONCLUSION

This article has shown that gas chromatography (GC)-based techniques continue to provide vital information to coating scientists and are standard analytical tools for the analysis of coatings and related ma-

terials. Many volatiles and semi-volatile compounds such as residual monomers, solvents, plasticizers, and low molecular weight additives such as mildewcides and antifoaming agents can easily be analyzed by GC. For higher molecular weight components, pyrolysis-GC/MS and related methods are applied. New technological advances in the areas of high-speed GC/MS and multidimensional GC systems and methods will probably become standard tools in coating analysis in the next few years. This is because such systems are now becoming more user friendly, (requiring less software) and more affordable than in the years past.

GLOSSARY

Cold injection: An injection that occurs at temperatures lower than the final oven temperature, usually at or below the solvent boiling point.

Column efficiency: The ability of a column to produce sharp, well-defined peaks.

Height equivalent to one theoretical plate, H: The distance along the column occupied by one theoretical plate: $H = L/N$.

Number of Theoretical Plates, N: Number of theoretical plates; $= 16 (t_r/w_b)2$

Resolution (R) – The quality of separation of two peaks. For two closely eluted peaks $R = (t_{r2} - t_{r1})/w_b$, 2—where the subscripts 1 and 2 refer to the first and second peaks. From N, k, and α, we get:

$R = (\sqrt{N}/4)[\alpha-1/\alpha](k_2/(k_2+1))$, where k_2 is the retention factor of the second peak. R incorporates both efficiency and separation.

Sensitivity: Signal output per unit concentration or per unit mass of analyte.

Split Ratio: Split flow rate/column flow rate.

Minimum detectability, D: $D = 2N/S$, where N = noise level and S = sensitivity.

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