High Pressure Liquid Chromatography

High pressure liquid chromatography (HPLC) is an established, standard analytical tool for the analysis of coatings and related materials. An extensive body of literature has been published in various analytical and related fields' journals on HPLC methods. These methods have been developed and used in the determination of small to very large molecules ranging from small organic impurities to polymer resins. In addition, fundamentals of HPLC and related methods have also been extensively covered in literature and the reader is encouraged to review them as needed. The objective of this article focuses mainly on the applications of HPLC and gel permeation chromatography (GPC) methods in the analysis of coatings.

INTRODUCTION

Liquid chromatography (LC) is probably the most commonly used method of separation and analysis of chemical compounds and ions in solution. Increased understanding of liquid chromatography since its invention in 1900 has led to fascinating and dramatic development and usage of the technique in a variety of applications. For example, instrumental advances, automation, and miniaturization of the technique have brought about the development of significant methods utilizing complex separation mechanisms, such as electrochromatography, supercritical fluid chromatography, microscale separations, and numerous powerful liquid chromatography techniques such as online and off-line liquid chromatography/nuclear magnetic resonance (LC-NMR), and very efficient multi-detector analysis systems for extremely complex analyses.

High pressure liquid chromatography (HPLC) is an analytical technique used for separation of low-to-moderate polarity of a variety of compounds of resins. The instrumentation for HPLC and size exclusion (SEC) or gel-permeation chromatography (GPC) is similar, but the columns differ. A schematic diagram of HPLC components is shown in Figure 1. HPLC components consist of the following: (a) solvent and/or solvent mixture, (b) solvents delivery system (pumps and controller), (c) sample delivery system (manual or automatic injection), (d) a column suitable for the separation of interest, (e) a detector system, and (f) a data system.

TYPES OF SEPARATION MECHANISMS IN LIQUID CHROMATOGRAPHY

There are numerous types of separation mechanisms in liquid chromatography. The most important ones include: affinity chromatography, ion chromatography, capillary electrophoresis, normal phase chromatography, reverse phase chromatography, supercritical fluid chromatography, and micellar chromatography.

Affinity Chromatography

Affinity chromatography is a technique that uses like-like interactions for current measurements (I) measured in milliamps, for a given voltage, a constant amount of current flows through the circuit and the voltage decreases as an element as its resistance increases. Molecules having electrical charge due to groups capable of dissociating electrolytically (for example, proteins), will migrate in an electrical field with a certain velocity and direction, which will depend on their electrical mobility. It has been shown that electrical mobility of a molecule is dependent on a safety of factors, such as electrical charge, coefficient of friction, shape, and molecular weight.

Capillary Electrophoresis

Capillary electrophoresis is a very important tool in the separation and identification of biomolecules. It also finds important application in polymer analysis. Normal Phase Liquid Chromatography

Normal phase liquid chromatography (NPLC) is a powerful separation technique, relies on the use of polar stationary phase and nonpolar liquid mobile phases for the separation of polar species. See the Type of Column Parameters section below.

Abbreviations and Acronyms

<table>
<thead>
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<th>Abbreviation</th>
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| FTRIR | Fourier Transform Infrared
| GPC | Gel Permeation Chromatography
| HPLC | High Pressure Liquid Chromatography
| LC | Liquid Chromatography
| MS | Mass Spectrometry
| MWD | Molecular Weight
| NMR | Nuclear Magnetic Resonance
| RPLC | Reverse Phase Liquid Chromatography
| SEC | Size Exclusion Chromatography
| TSS | Total Suspended Solids
| UV | Ultraviolet

| Table 1—Anions and Cations that can be Separated and Quantified |
|--------------|------------------|
| Anions | Cations |
| Bromide | Br⁻ | Ammonium | NH₄⁺ |
| Chloride | Cl⁻ | Calcium | Ca²⁺ |
| Fluoride | F⁻ | Iron | Fe³⁺ |
| Iodide | I⁻ | Iron | Fe²⁺ |
| Nitrate | NO₃ | Magnesium | Mg²⁺ |
| Nitrite | NO₂⁻ | Sodium | Na⁺ |
| Phosphate | PO₄³⁻ | Zinc | Zn²⁺ |
| Sulfate | SO₄²⁻ | Sulfate | SO₄²⁻ |

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High Pressure Liquid Chromatography
In Coatings Analysis

by Francis V. Acholia, Rohm and Haas Company

High pressure liquid chromatography (HPLC) is an established, standard analytical tool for the analysis of coatings and related materials. An extensive body of literature has been published in various analytical and related fields’ journals on HPLC methods. These methods have been developed and used in the determination of small to very large molecules ranging from small organic impurities to polymer resins. In addition, fundamentals of HPLC and related methods have also been extensively covered in the literature and the reader is encouraged to review them as needed. The objective of this article focuses mainly on the applications of HPLC and gel permeation chromatography (GPC) methods in the analysis of coatings.

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High pressure liquid chromatography (HPLC) is an analytical technique used for separation of low-to-moderate on a variety of compounds of resins. The instrumentation for HPLC

(Types of separation mechanisms in liquid chromatography)

There are numerous types of separation mechanisms in liquid chromatography. The most important ones include: affinity chromatography, ion chromatography, capillary electrophoresis, normal phase chromatography, reverse phase chromatography, supercritical fluid chromatography, and microscale chromatography.

Affinity Chromatography

Affinity chromatography is a technique that uses like-like interactions for (d) a column suitable for the separation of interest, (e) a detector system, and (f) a data system.

Figure 1—Schematic diagram of HPLC components.

Effective separation and analysis of sample components in solution. The column is designed to retain specific or similar analytes while allowing everything else through the column. The retained species can then be selectively eluted from the column by appropriate solvents. A schematic example of affinity chromatography is shown in Figure 2.

Ion Chromatography

Ion chromatography is a liquid chromatography method that can be used for the separation and quantification of anions and cations. For example, anions and cations that are separated and quantified are given in Table 1. A schematic ion separation and identification is shown in Figure 3.

In the context of this article, ion chromatography is used in the determination of acid species in the acid/neutral decomposition of polymeric materials and ionic contamination in polymers and paints.

Capillary Electrophoresis

Capillary electrophoresis is a very important tool in the separation and identification of ions. It also finds important application in polymer analysis.

Normal Phase Liquid Chromatography

Normal phase liquid chromatography (NPLC) is a powerful separation technique, relies on the range of polar stationary phases and nonpolar liquid mobile phases for the separation of polar species. See the Type of Column Phases section below.

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</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>LC</td>
<td>Liquid Chromatography</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>RPLC</td>
<td>Reverse Phase Liquid Chromatography</td>
</tr>
<tr>
<td>SEC</td>
<td>Size Exclusion Chromatography</td>
</tr>
<tr>
<td>TDA</td>
<td>Trimethylamine Dihydrogen Phosphate</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
</tbody>
</table>

Table 1—Anions and Cations that can be Separated and Quantified

<table>
<thead>
<tr>
<th>Cation</th>
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<tbody>
<tr>
<td>Acids</td>
<td>Bromide...Br⁻</td>
</tr>
<tr>
<td></td>
<td>Chloride...Cl⁻</td>
</tr>
<tr>
<td></td>
<td>Fluoride...F⁻</td>
</tr>
<tr>
<td></td>
<td>Nitrate...NO₃⁻</td>
</tr>
<tr>
<td></td>
<td>Nitrite...NO₂⁻</td>
</tr>
<tr>
<td></td>
<td>Phosphate...PO₄³⁻</td>
</tr>
<tr>
<td>Sulfate...SO₄²⁻</td>
<td></td>
</tr>
</tbody>
</table>
Chromatography

The identification of the species is made against known references. Detection limits can be as low as parts per billion (ppb) levels.

Microscale Liquid Chromatography

Microscale liquid chromatography is simply the miniaturization of liquid chromatography technique. The main advantages are the significant reduction of solvents, shorter analysis times, and overall improved sensitivities.

TYPE OF COLUMN PHASES

There are two main types of phase separation: (1) the normal phase HPLC, which consists of a polar column material and relatively nonpolar solvents, and (2) reversed phase HPLC which consists of a nonpolar column material and relatively polar solvents.

Reversed phase HPLC is the preferred type of HPLC as it has proven to be the best for analysis of many types of resins. The most common column packing materials are nonpolar hydrocarbons, C₆, C₈, and phenyl bonded phases columns. The most common polar solvents for resins include acetonitrile (ACN)/water, methanol/water, and tetrahydrofuran (THF)/water. They are usually used in the gradient elution mode because they allow one to start with low content of organic component in the eluent (ACN or THF) and then, more strongly retained components will move faster for improved resolution.

INJECTORS FOR HPLC

Samples are injected into the HPLC via an injection port. The injection port of an HPLC commonly consists of an injection valve and the sample loop. The sample is typically dissolved in the mobile phase before injection into the sample loop. The sample is then drawn into a syringe and injected into the loop via the injection valve. A rotation of the valve rotor closes the valve and opens the loop in order to inject the sample into the stream of the mobile phase. Loop volumes can range between 10 µl to over 500 µl. In modern HPLC systems, the sample injection is typically automated.

DETECTORS

Detection methods are critical to the successful application of HPLC methods in separation. Some of the conventional and newer detection methods are: UV/Vis, fluorescence, conductivity, and luminescence. Fourier transform infrared spectroscopy (FTIR), mass spectrometry (MS), and nuclear magnetic resonance (NMR). Exhaustive discussion of these newer detection methods has been reviewed in the literature.

An example of HPLC Run conditions for polymer emulsion and/or paints can be as follows:

**SAMPLE PREPARATION:** The sample can be dissolved in THF at roughly 1% (w/w) and centrifuged at 40,000 rpm for 15 minutes. The supernatant is then filtered through 0.2 µm filters prior to injection on the HPLC system.

**CHROMATOGRAPHIC CONDITIONS:**

- Column: PLRP-S 400Å 8µ analytical column (Polymer Labs), 4.6 mm x 15 cm, 8 µm dₘ
- Mobile Phase: 25:75 THF/methanol initially. Linear gradient to 75:25
- Sample loop: 10 µl
- Flow Rate: 1.0 ml/min
- Injection Volume: 10 µl
- Temperature: Ambient
- Detector 1: UV @ 260 nm
- Detector 2: Evaporative Light Scattering Detector (ELSD)

**APPLICATIONS**

Raw materials that go into the manufacture of paints are sometimes more complex than the supplier or formulators realize. Components such as surfactants may be sold as "pure" or within certain specifications but may often contain several by-products that may play an important role in the chemistry of the formulated paint.

**ANALYSIS OF RESIDUAL ALCOHOLS AND ALKANES IN SURFACTANTS:** Figure 4 shows HPLC analysis of two batches of surfactants for residual alcohol impurities. In Figure 5, the HPLC of two batches of a sulfated surfactant that are supposed to be chemically identical are presented.

**ANALYSIS OF Binder Type in Fully Formulated Paint Systems:** Compositional analysis of paints can be a daunting task for analysts. The paint components can be dissolved in a 9:1 mixture of THF/petroleum ether. The THF extract is separated by normal phase HPLC (polar column and nonpolar solvents) or reverse phase HPLC (nonpolar column and polar solvents). For example, a failed coating can be extracted by THF; however, depending on the composition of the formulated paint, analysts may encounter very challenging situations where answers to specific questions may depend on many variables. For example, the use of organic opacifiers has many benefits including increased opacity, low binder demand, and partial TiO₂ replacement, which significa...
Figure 3—Schematic representation of anion separation and identification by ion chromatography. The identification of the species is made against known references. Detection limits can be as low as parts per billion (ppb) levels.

F σ Cl σ Br σ NO3 σ PO4 σ
Response on Chromatography
Retention Time

Inmm. and a detector. The flame ionization detector (FID) is most common, but other GC or LC detectors can also be used. SFC finds many applications in polymer additives analysis.

Microscale Liquid Chromatography

Microscale liquid chromatography is simply the miniaturization of liquid chromatography technique. The main advantages are the significant reduction of solvents, shorter analysis times, and overall improved sensitivities.

Type of Column Phases

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Detectors

Detection methods are critical to the successful application of HPLC methods in separation. Some of the conventional and newer detection methods are: UV/Vis, fluorescence, conductivity, and mass spectroscopy (MS). Mass spectroscopy allows the determination of the molecular weight of the compound. DAD is one of the most commonly used methods in HPLC, and it is suitable for all types of samples.

Applications

Raw materials that go into the manufacture of paints are sometimes more complex than the surrogates or formulations realize. Components such as surfactants may be added as "pure" or within certain specifications but may often contain several by-products that may play an important role in the chemistry of the formulated paint. The following examples illustrate how HPLC can be used for raw materials and fully formulated paints.

Analysis of Residual Alcohols and Alkenes in Surface Coatings: Figure 4 shows HPLC analysis of two batches of surfactants for residual alcohol impurities. In Figure 5, the HPLC of two batches of a sulfated surfactant that are supposed to be chemically identical are presented.

Analysis of Binder Type in Fully Formulated Paint Systems: Composition analysis of paints can be a daunting task for analysts. The paint components can be dissolved in an appropriate solvent (THF) and separated by either normal phase HPLC (polo column and nonpolar solvents) or reverse phase HPLC (nonpolar column and polar solvents). For example, a failed coating can be identified by THF; however, depending on the composition of the formulated paint, analysis may encounter very challenging situations where answers to specific questions may depend very much on many variables. For example, the use of organic solvents has many benefits including increased opacity, low binder demand, and partial TiO₂ replacement, which significantly

Figure 5—HPLC chromatogram of two batches of a sulfated surfactant that are supposed to be chemically identical. Surfactant A appears to have significantly higher levels of C₅-C₆ and C₇-C₉ hydrocarbons when compared to surfactant B (printed with permission from Dan Dohnemier, unpublished).

THF/methanol over 35 min. Back to initial conditions in 5 min. Equilibrate for 10 min.

Flow Rate: 1.0 ml/min
Injection Volume: 10 μl
Column Temperature: Ambient
Detector 1: UV @ 270 nm
Detector 2: Evaporative Light Scattering Detector (ELSD)

Applications

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GEL PERMEATION CHROMATOGRAPHY

Gel permeation chromatography (GPC), or size exclusion chromatography (SEC), is a branch of HPLC whose primary role is to provide molecular weight data on polymers and resins. GPC allows polymer synthesis chemists and paint formulators and application scientists to isolate and characterize low molecular weight additives and medium-to-high molecular weight polymers and resins in polymeric systems.

In GPC, the two most common detectors are ultraviolet (UV) and refractive index (RI). Only solutes that absorb in the UV region (with UV chromophore) can be detected by UV detection; for example, aromatic compounds, or conjugated double bonds. If a polymer has no UV chromophore or is unknown, the RI detector is the best choice. The RI detector functions by monitoring the change in refractive index between the pure mobile phase and that containing the sample. The difference is the signal of the peak(s) of elution.

In GPC, the column is packed with a semi-rigid gel or small organic particles, which function as a physical barrier for separating molecules of different molecular weights. The key function of the stationary phase is to allow the polymer molecules to interact with the solvent molecules in such a way that these molecules that have more physical interactions with the pores of the column packing will take longer to elute than those that have no physical interaction with the pores. For example, high molecular weight polymers will elute faster. The separation mechanism in a GPC column is represented in Figure 8.

It can be schematically shown that the smaller molecules can fit into the small pores and therefore take longer to elute through the column. The larger molecules, on the other hand, due to their size, are unable to enter the pores and simply travel around the gel particles on their way out. Thus, the large polymer molecules are the first to elute out, followed by the medium size, and finally by the smaller molecules. It is important to point out that GPC also separates molecules according to their hydrodynamic volume.11

In order for the GPC data to be useful, it must be calibrated with polymers of known molecular weight. Polystyrene standards are often used because they are readily available over a wide range of molecular weights.

APPLICATIONS IN FAILURE ANALYSIS

Coatings scientists are always interested in determining the composition of polymers as they largely determine the chemical resistance properties of coatings. GPC is one of the best methods that can be used to measure the molecular weight of polymers in coatings. In order to accomplish this, the polymer must be isolated from the paint by using an appropriate solvent. In the example shown in Figure 9, the polymer was isolated from a paint by extraction in THF followed by centrifugation to remove the pigment and other THF insolubles.

In coatings failure analysis, GPC can provide data to determine whether the failing paints conform to specification by comparing and finger-printing failed paint to a control. Coating failures due to polymer decomposition can easily be detected. For example, GPC performed on a failing and on control paints showed a dramatic difference in molecular weight, with the failing samples being lower than the control.12 There are numerous examples in the literature where GPC can be used to investigate coating failures.13 It is important to point out that GPC has two major limitations in coating analysis; it cannot be used on insoluble coating samples and it cannot provide chemical information. However, the chemical information limitation can be overcome by interfacing GPC to a variety of chemically sensitive tools, such as FTIR, NMR, and MS.12

SUMMARY

A general overview of the application of HPLC techniques for analysis of paints and related materials has been presented. We have discussed how HPLC can be used for raw materials and for fully formulated paint analysis. GPC has been demonstrated as one of the best methods that can be used to measure the molecular weight of polymers in coatings and coatings failure analyses. However, these methods require that the polymer or isolated coating, John Wiley and Sons, New York, NY. pp. 206, 2001.


References


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