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PYROLYSIS GC/MS AS A METHOD FOR QUALITY AND MANUFACTURING CONTROL

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PYROLYSIS-GC/MS AS A METHOD FOR QUALITY AND MANUFACTURING CONTROL

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Abstract

Adhesive manufacturers depend on purchased adhesives, polymers, resins, films and organic additives. What is the best method for understanding variations in the quality of purchased and finished products? Common analytical methods used in an adhesive laboratory, such as DMA, GPC, TGA and FT-IR, can provide general information about raw materials or finished products, but they are often unable to detect subtle batch-to-batch chemical variation. By using pyrolysis coupled with GC/MS, even minor differences can become apparent. Pyrolysis-GC/MS is an important tool used in the quality control of incoming raw materials, the evaluation of raw material substitutions and in troubleshooting finished products.

Introduction

A stable, uniform raw material stream is critical for insuring a uniform end product. This is true for both the manufacturers of the basic starting blocks of pressure sensitive adhesives such as resins, polymers, films and papers, and for the finished adhesives and tapes themselves. After all, ensuring batch-to-batch consistency is what quality control is all about.

Inconsistency can occur for a number of reasons. For example:

If you are a vendor of raw materials for pressure sensitive adhesives you may discover:

1. Variations in your natural raw material supply:
    a. Different forest = different trees = different quality of resin or paper
    b. Different section or location of a mine equals different quality of filler
2. Variations in your industrial feed stocks
    a. Shortage of raw material feedstock (C5s for example)
    b. You've changed your own raw material supplier in order to obtain a less expensive or more readily-available feedstock

If you are a manufacturer of finished pressure sensitive adhesives or tapes you may find:

1. Your vendor has stopped making a preferred raw material
2. Your preferred raw material has been banned
3. You think you've found a less expensive source for a raw material
4. You can't get a raw material due to a shift in supply and demand
5. Your QC department has detected a strange change in the quality of an adhesive, film or paper backing and you suspect something in your raw material supply has changed.

Testing Your Raw Material Supply

There are many useful analytical techniques for monitoring a raw material supplies. One of the most common is **Fourier Transform InfraRed Spectroscopy (FT-IR)**. FT-IR is a method of obtaining infrared spectra by first collecting an interferogram of a sample, and then performing a Fourier Transform (FT) algorithm on the interferogram to obtain the spectrum. This infrared spectrum is a "fingerprint" of the sample that can be used for comparison purposes. FT-IR systems are fast, non-destructive and easy to operate. They are not without shortcomings, however. It can be difficult to detect subtle differences between samples and identify additives when the levels in the sample are less than 5%. A good quality search library of commercial raw materials and formulations is critical and takes time to develop.

Pyrolysis–Gas Chromatography/Mass Spectrometry (GC/MS) is a method of chemical analysis in which the sample is thermally decomposed in an inert atmosphere to produce smaller gas molecules that can be separated by gas chromatography and detected using mass spectrometry. At a given pyrolysis temperature, the input of thermal energy will cause chemical bonds to break in a reproducible manner that depends on the structure of the molecule. The gas chromatograms/pyrograms from the pyrolysis of polymers and resin are also chemical "fingerprints" that can be used for quality control purposes. Mass spectrometry can then be used to identify the *individual peaks* in the chromatogram. This is particularly useful when dealing with pressure sensitive adhesives that are mixtures of polymers or resins, unknown contaminants and trace level additives [1].

In this paper a number of examples will be used to compare pyrolysis-GC/MS analysis to FT-IR as a way to understand variations in the quality of raw materials and finished products.

The following examples are a cross-section of the type of raw material analyses that occur daily in a production or R&D laboratory.

The analytical instruments used were:

FT-IR:

All samples were analyzed in absorbance mode on a ThermoNicolet Nexus 670 FT-IR equipped with a Golden Gate™ Diamond ATR.

Pyrolysis-GC/MS:

All samples were pyrolyzed at 750°C using a CDS Pyroprobe 5000 Series equipped with a 5250-T Autosampler. The pyrolysis gases were analyzed on an Agilent 7890/5975C GC/MS using a 5% phenyl capillary column.

Example 1

Problem: The supply of a raw material has become constrained.

Two polyterpene resins were submitted for analysis when the supply of the preferred resin became constrained. A different supplier recommended their polyterpene resin as a substitute. Can the new resin be used as a 'drop-in' replacement for the old resin?

FT-IR Analysis

The FT-IR spectra of the two resins were very similar. The substitute resin is an excellent spectral match to the control resin when searched against it in the FT-IR spectral library (98.6% match).

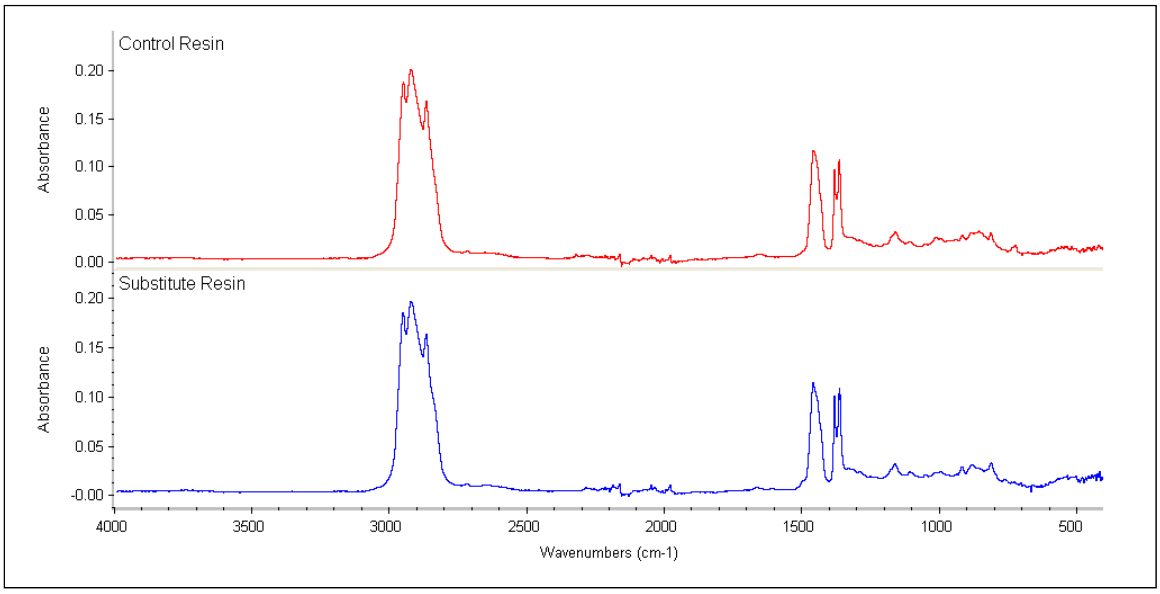

Figure 1: FT-IR Comparison of Two Polyterpene Resins

Pyrolysis-GC/MS Analysis

When the resins were examined using pyrolysis-GC/MS, a significant difference was detected. The main pyrolysis fragment (pyrosate) of the polyterpene resin was the same in both samples: β-phellandrene. But the substitute resin contained a number of fragments from the pyrolysis of high molecular weight naphthenic compounds. While these compounds may not necessarily affect the behavior of the resin, the presence of naphthalenes can have other environmental consequences.

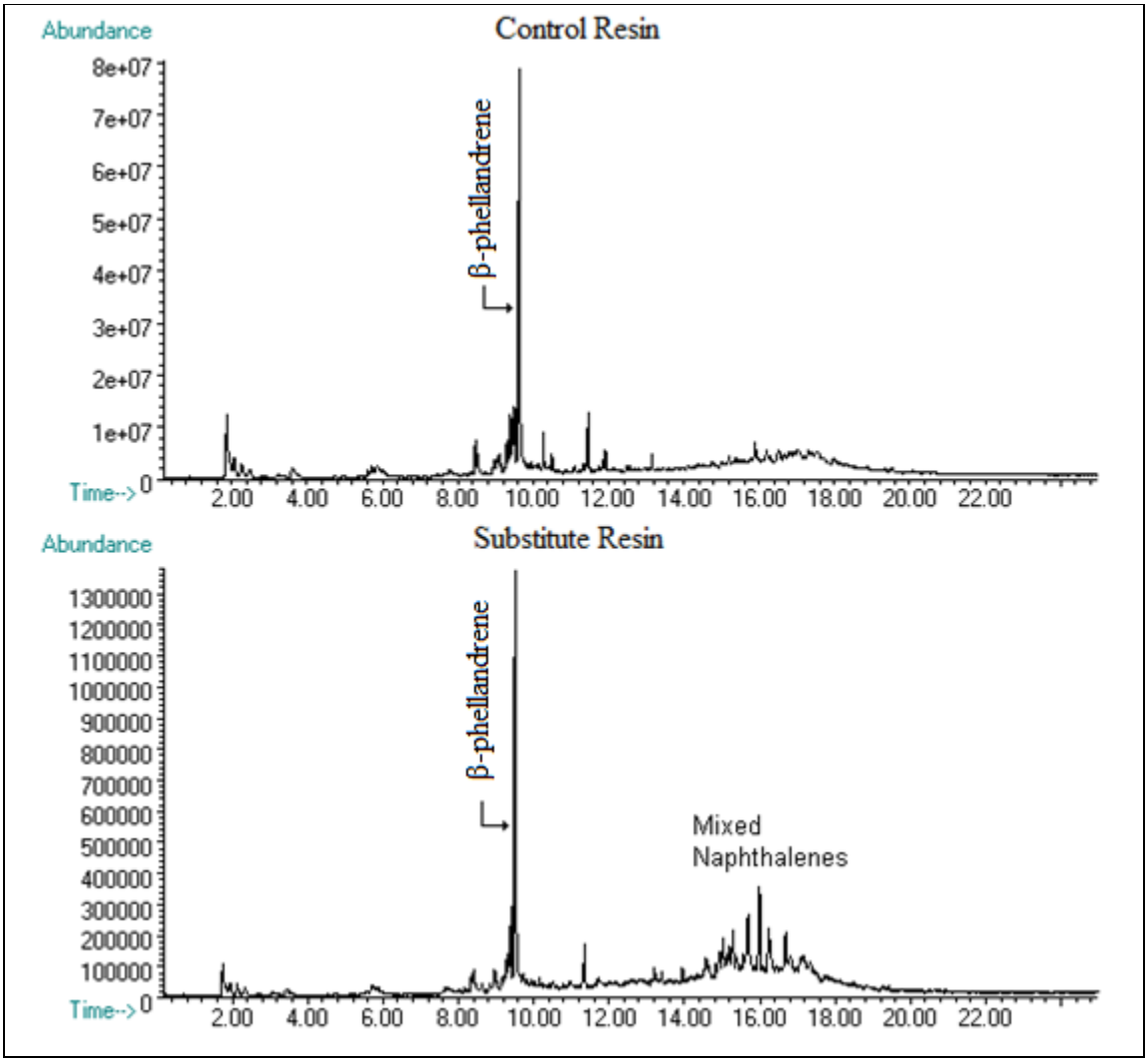

Figure 2: Pyrolysis-GC/MS Comparison of Two Polyterpene Resins

Example 2

Problem: You're looking for a less expensive supply for rosin esters.

With the constant pressure to lower costs, a large amount of analytical resources can be devoted to screening lower-cost raw materials. Rosin esters are commonly used tackifying resins in pressure sensitive adhesives. Three types of rosin are used to manufacture resins: gum rosin (from pine gum), wood rosin (from pine stumps) and tall oil rosin (from the crude tall oil left over from the Kraft pulping process). Rosin esters are produced from a blend of many types of rosin acids, including abeitic and pimaric acids. They can also be stabilized using disproportionation and hydrogenation to remove unstable double-bonds. [2, 3]

FT-IR Analysis

In the example below, two rosin ester samples were compared to a control standard. By examining the three different spectra, some subtle differences can be noted between the samples, but nothing that would clearly distinguish one from the other.

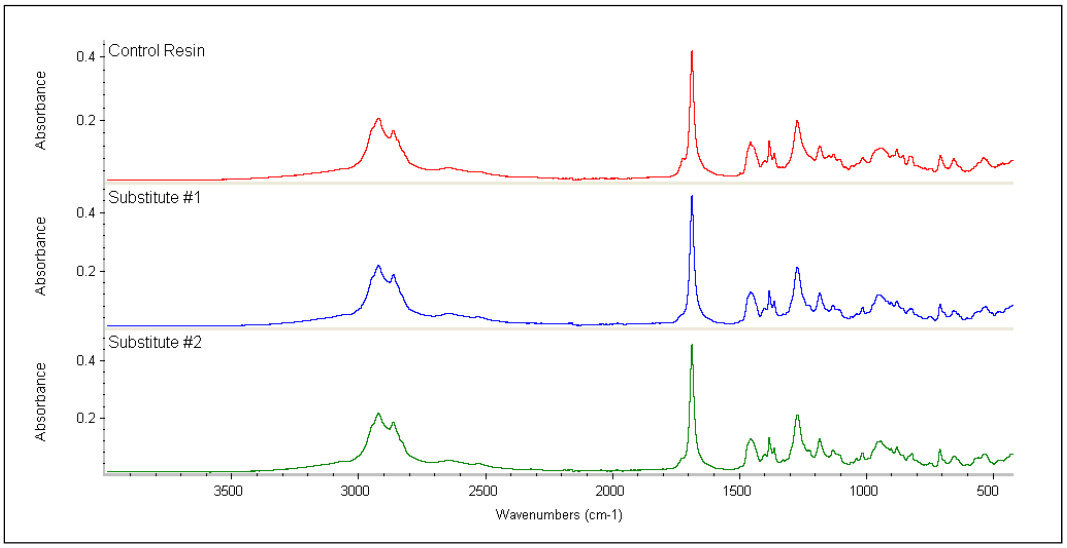

Figure 3: FTIR Comparison of Three Rosin Esters

Pyrolysis-GC/MS Analysis

Unlike the FT-IR spectral analysis, the pyrolysis-GC/MS analysis of the samples shows three distinct rosin ester chromatograms. The diterpenes in Substitute Resin #1 may indicate a mixture of gum and wood rosins, since terpenes and wood rosin can both be obtained from stump extraction. The rosin acids in Substitute Resin #2 are different from the abeitic acid seen in the first two samples and could indicate the blending of a crude tall oil.

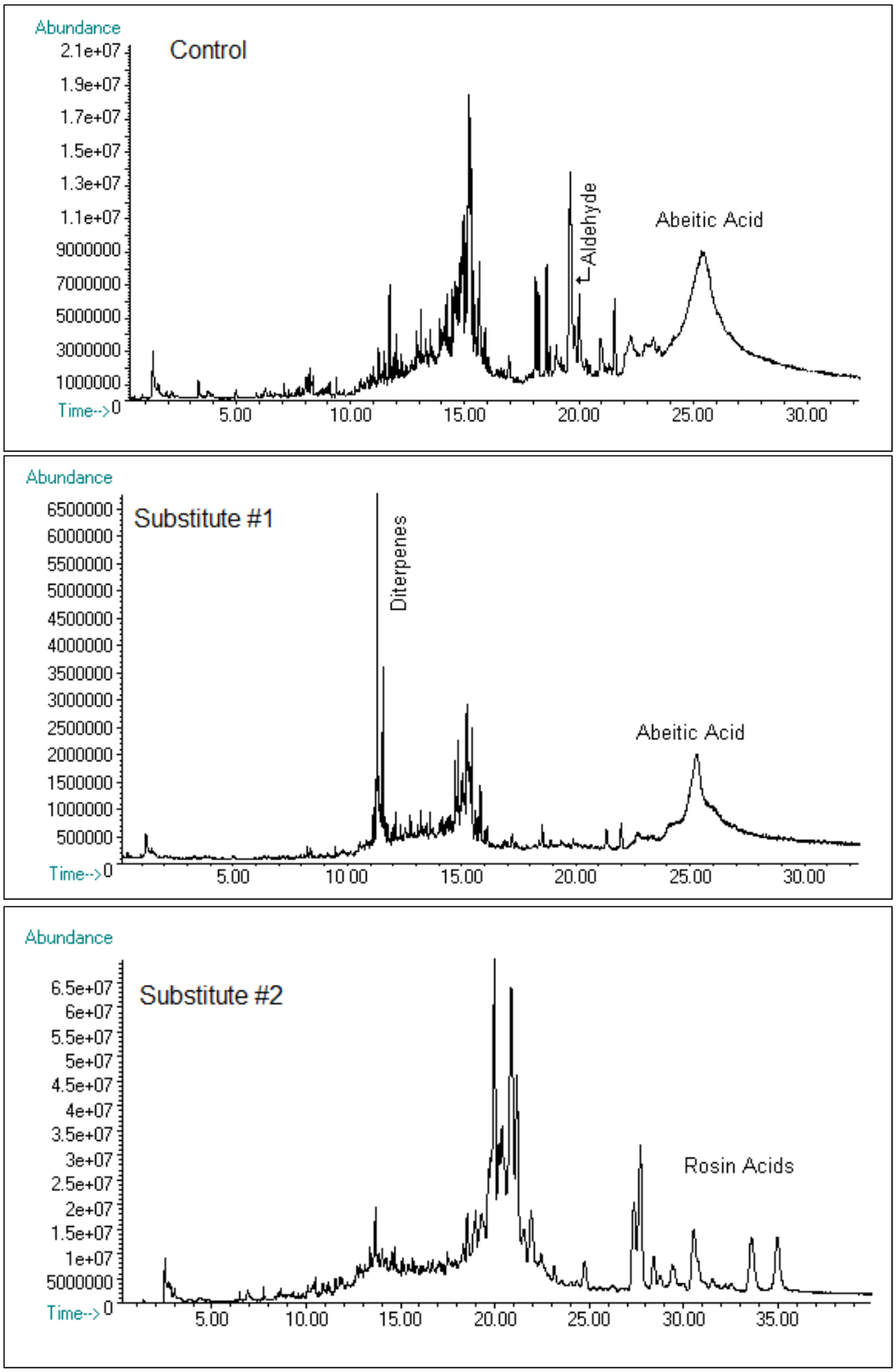

Figure 4: Pyrolysis-GC/MS Comparison of Three Rosin Esters

Example 3

Problem: The QC department detects a change in your backing. Has the paper or saturant changed?

A. Measuring variation in paper

The variation in paper used as backing for tapes, or in the construction of paper products designed to be sealed by PSAs, can be a critical factor in the success or failure of a product. What is the source of the wood? Are the trees grown in cold or tropical conditions? What is the species of wood? Does the paper contain any recycled material?

FT-IR Analysis

Unfortunately, the FT-IR spectra of untreated paper samples only tend to show that they contain cellulose – a not very helpful result. In the image below, two very different samples of paper have nearly identical FT-IR spectra.

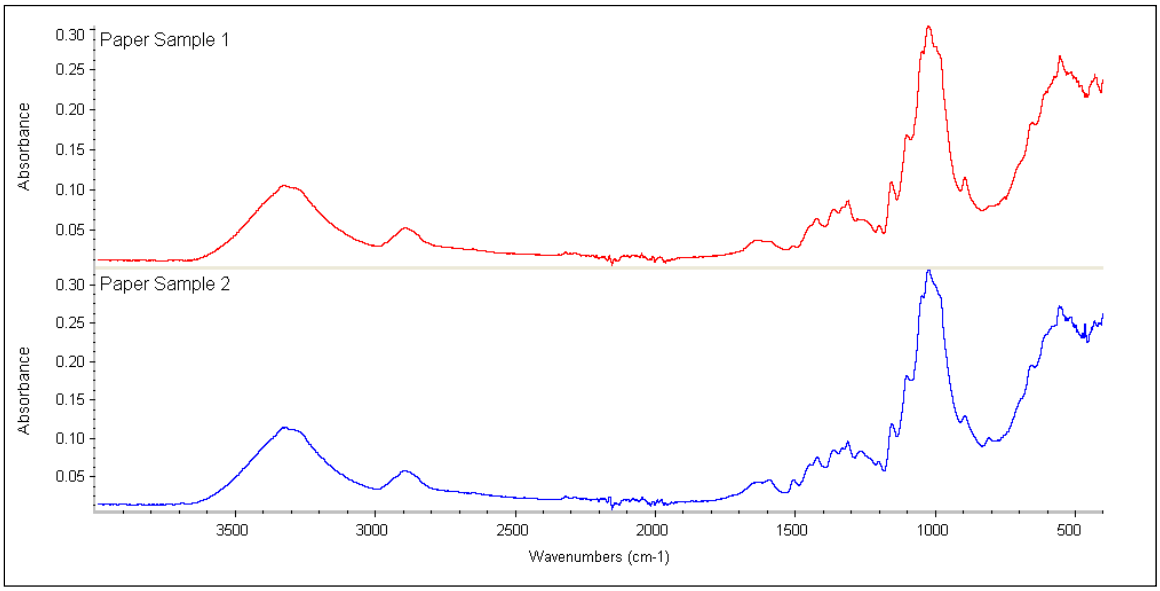

Figure 5: FT-IR Comparison of Two Paper Samples (Cellulose)

Pyrolysis-GC/MS Analysis

The lignin content of paper from different species of wood has been extensively studied [4-10]. In recent years, the amount of fibers from Asian woods like eucalyptus has begun to creep into the domestic paper supply, displacing paper made from native pine trees. Lignin is a complex organic compound that binds to cellulose fibers and hardens and strengthens the cell walls of plants. It is the chief non-carbohydrate constituent of wood.

In the chromatograms below, major differences between two identical appearing papers can be seen. One of the papers is very low in lignin content, while the other is much higher in lignin content and has a more complex distribution of lignins. This may represent two or more different species of wood fibers used in the second paper.

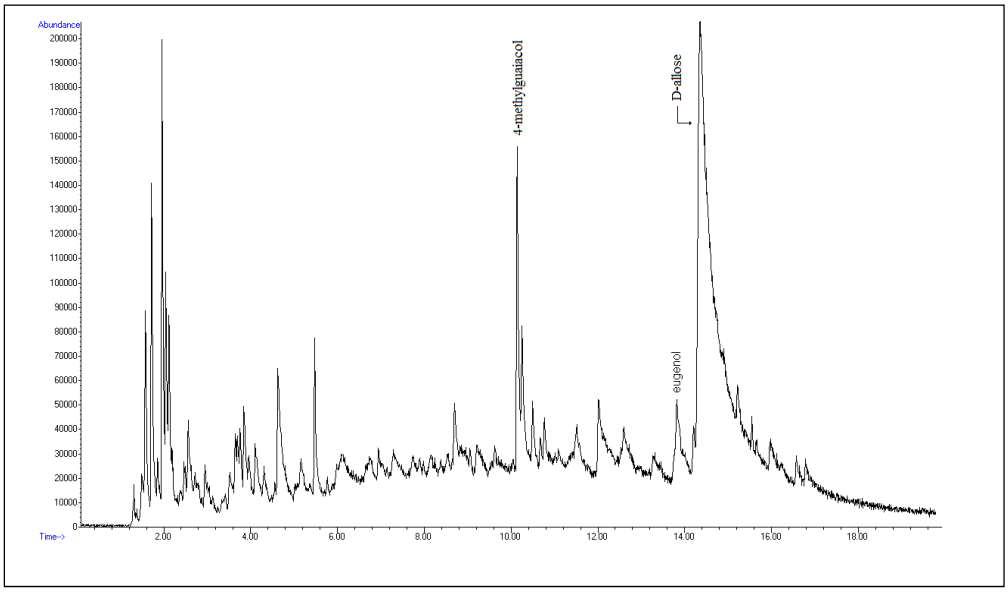

Figure 6: Pyrolysis-GC/MS of a Low Lignin Paper

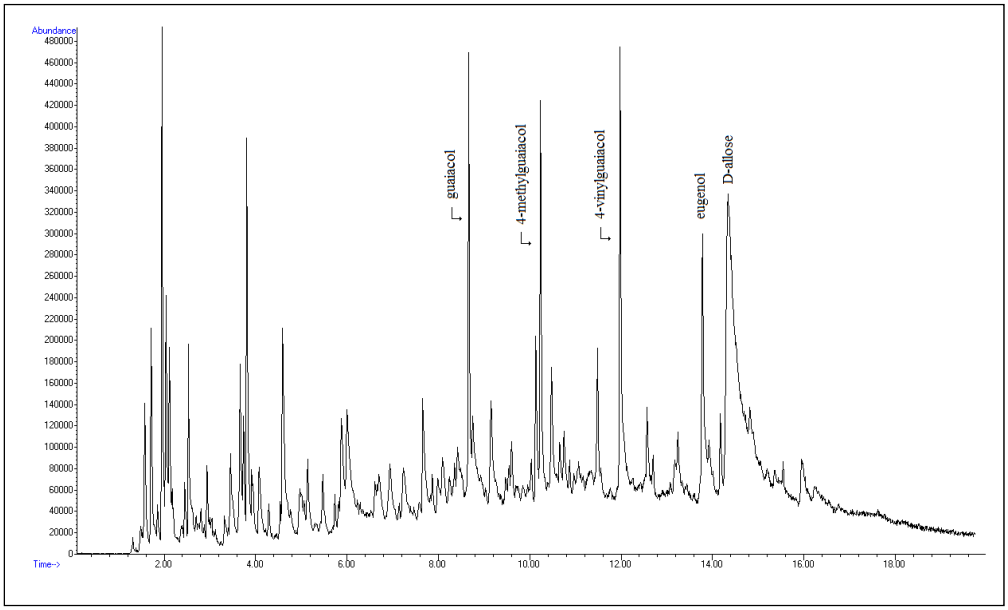

Figure 7: Pyrolysis-GC/MS of a High Lignin Paper

B. Measuring variation in paper saturant

Typically, the paper is saturated with a latex emulsion such as styrene butadiene (SBR), polyvinyl acetate, vinyl acrylate, polyvinyl chloride, or an acrylic emulsion. Understanding the nature of the saturant, particularly when purchasing an already saturated paper, can be crucial to understanding variations in a backing.

FT-IR Analysis

As with the FT-IR analysis of plain paper samples, the absorbance of cellulose dominates the spectra of the saturated samples, obscuring peaks with low wavenumbers like butadiene and styrene.

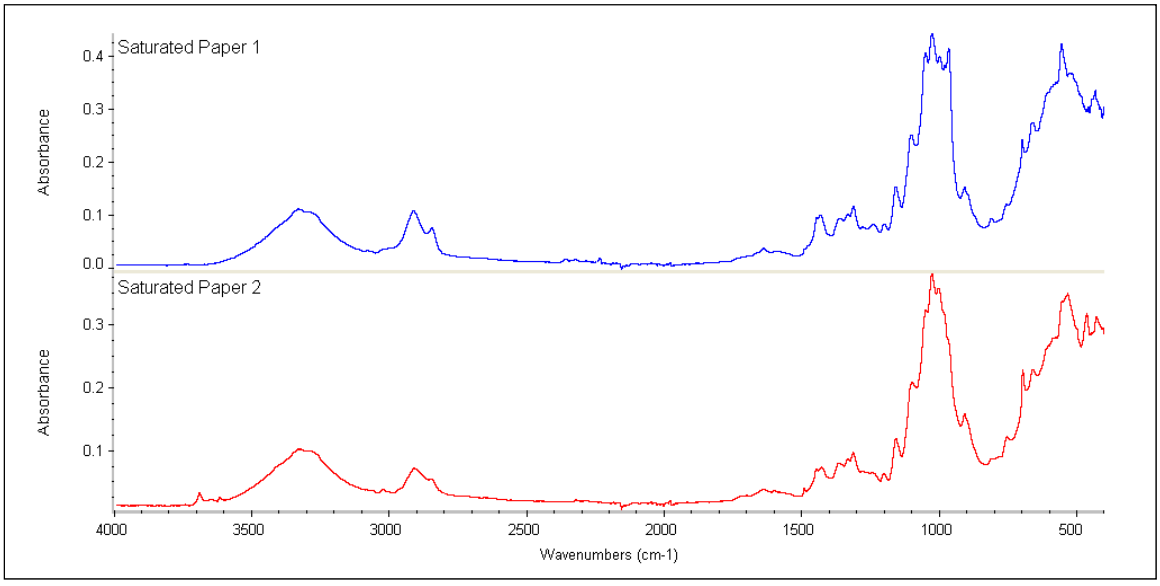

Figure 8: FT-IR of Two Saturated Paper Samples

Pyrolysis-GC/MS Analysis

The main pyrolysis products of SBR are the butadiene monomer (1, 3-butadiene) and dimer (4-ethenyl cyclohexene), styrene and smaller fragments generated from styrene (toluene, xylene). [11, 12]. In the chromatograms shown below, the first sample contains not only SBR, but smaller amounts of polyvinyl chloride and acrylon. There also appears to be a small amount of resin in the saturant or paper. In the second sample, the saturant is just SBR.

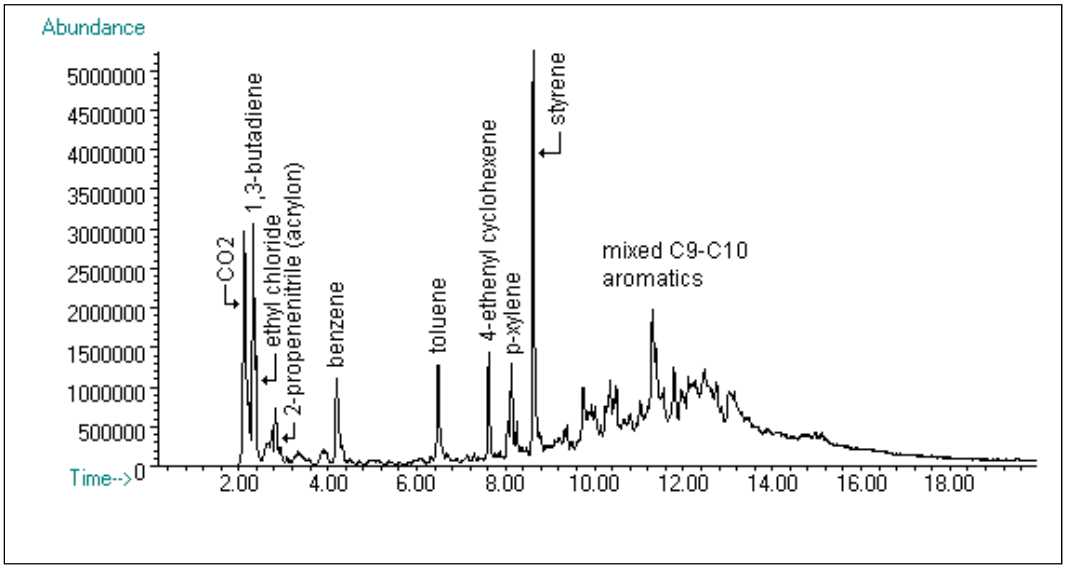

Figure 9: Gas Chromatogram of Saturated Paper 1

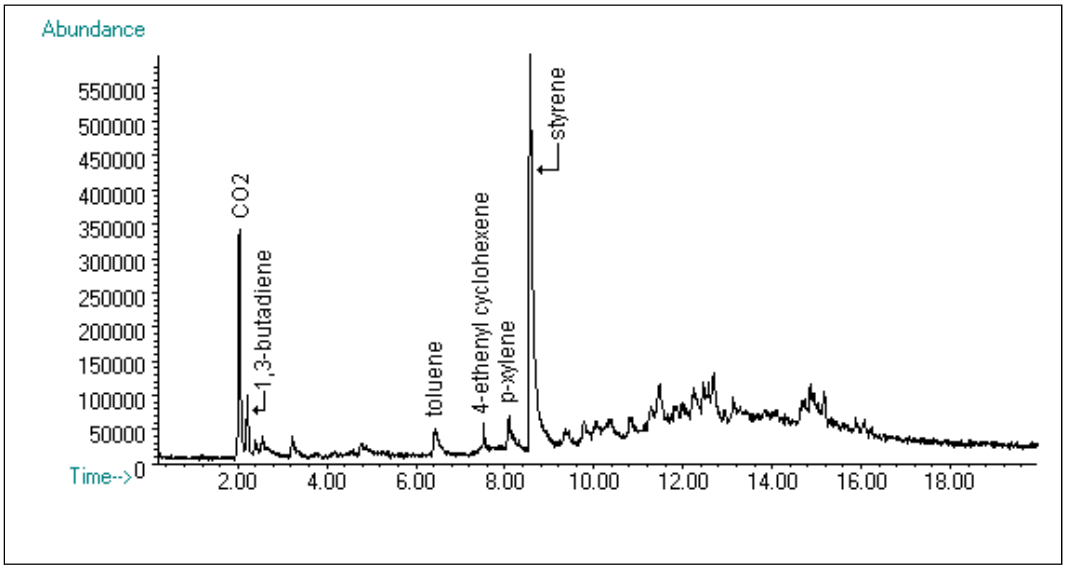

Figure 10: Gas Chromatogram of Saturated Paper 2

Example 4

Problem: Your raw material has just been banned.

C8 fluoropolymer emulsions were once used in coatings. Then C8 fluoropolymers were banned by the EPA under the 2010/15 PFOA Stewardship Program. There was concern that perfluorooctanoic acids would bioaccumulate in the body and eventually become toxic. When supplies became severely limited, C6 fluoropolymers were submitted for analysis as possible substitutes.

FT-IR Analysis

In this case, the FT-IR shows a clear difference between the Control C8 fluoropolymer and the C6 substitute.

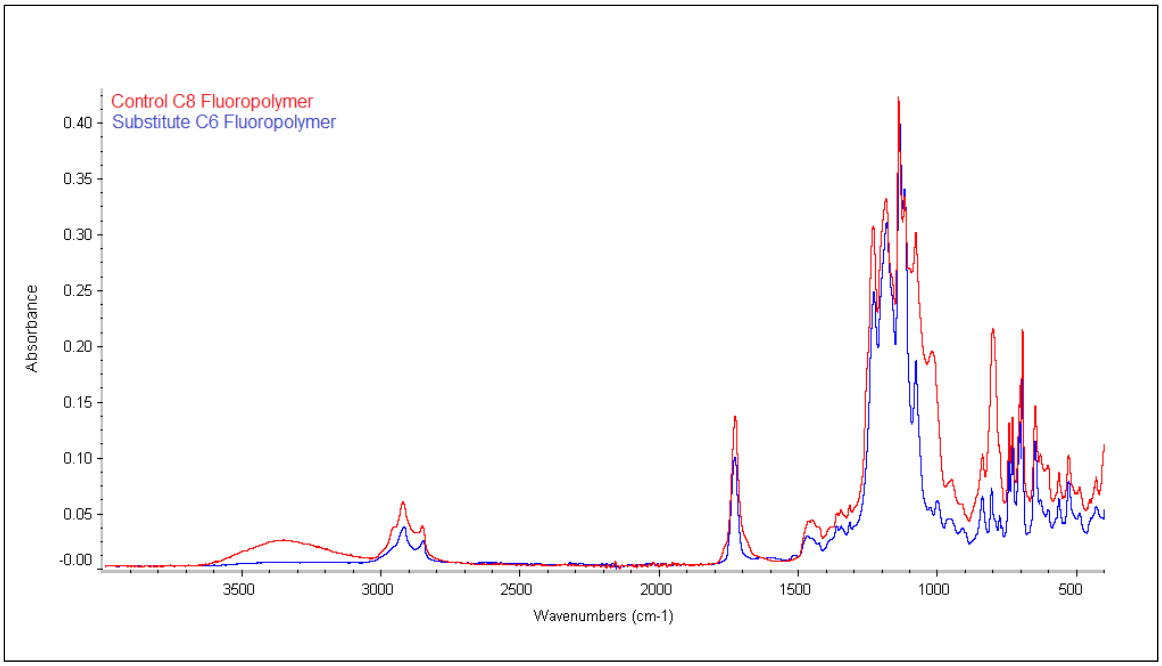

Figure 11: FT-IR Overlay comparing C8 and C6 Fluoropolymers

Using the FT-IR's spectral subtraction feature, the difference between the two samples can be determined. Based on the subtraction spectrum, the Control C8 sample not only contained the C8 fluoropolymer, it also contained a silicone additive.

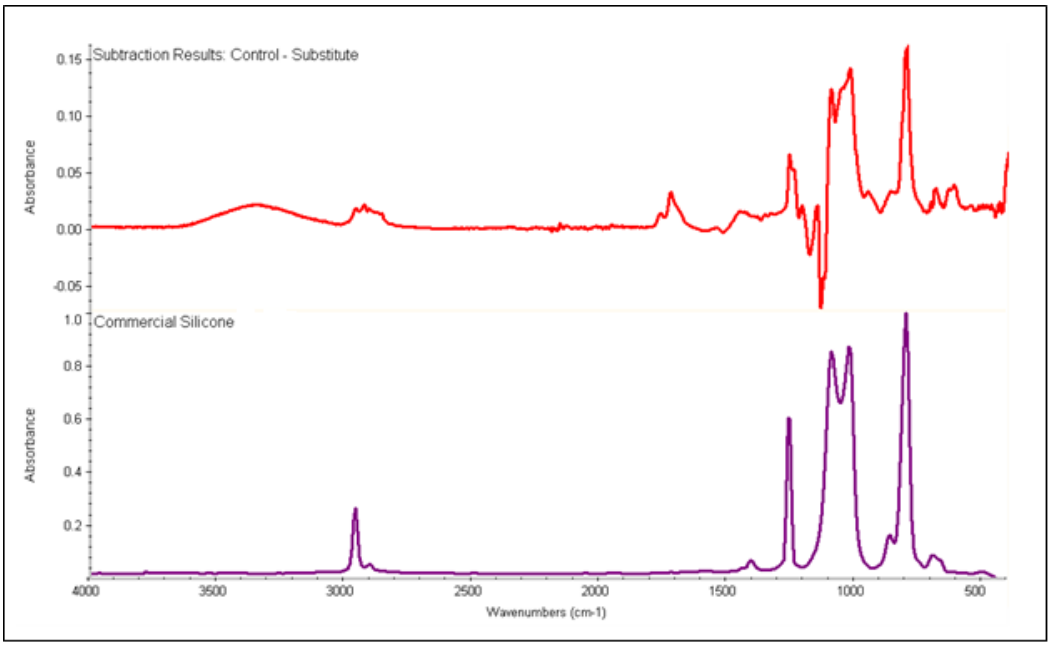

Figure 12: Spectral Subtraction of C6 Fluoropolymer for C8 Control

Pyrolysis-GC/MS Analysis

As with other types of polymers, fluoropolymers will fragment in accordance with their chemical structures [13]. The differences seen in the chromatograms below are not structural; they are due to the different additives used in the coatings.

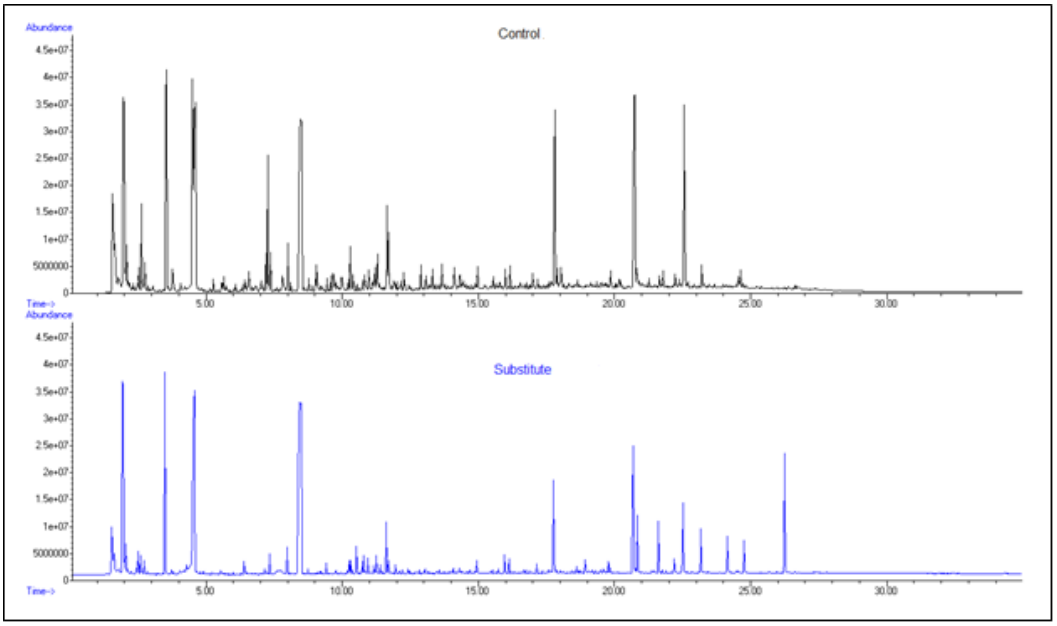

Figure 13: Gas Chromatograms of Control C8 vs. Substitute C6 Fluoropolymer Releases

To distinguish between the additives in the two samples, Selected Ion Monitoring (SIM) was used to increase the detection sensitivity of the additive peaks. SIM is a mass spectrometry scanning mode in which only a limited mass-to-charge ratio range is scanned, as opposed to the full spectrum range. This has the effect of increasing sensitivity by focusing the detector on the compound in question. The Control C8 sample showed the pyrolysis fragments of a silicone additive as was detected on the FT-IR. The C6 substitute showed the pyrolysis fragments of a methyl acrylate additive – which was not detected by FT-IR.

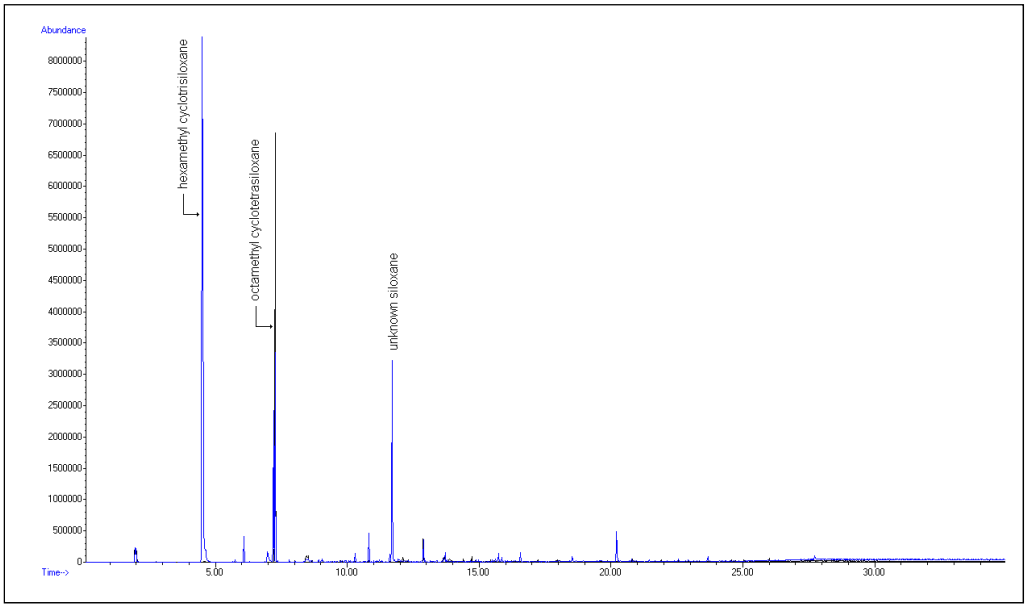

Figure 14: SIM of Control C8 Fluoropolymer showing Multiple Siloxane Peaks

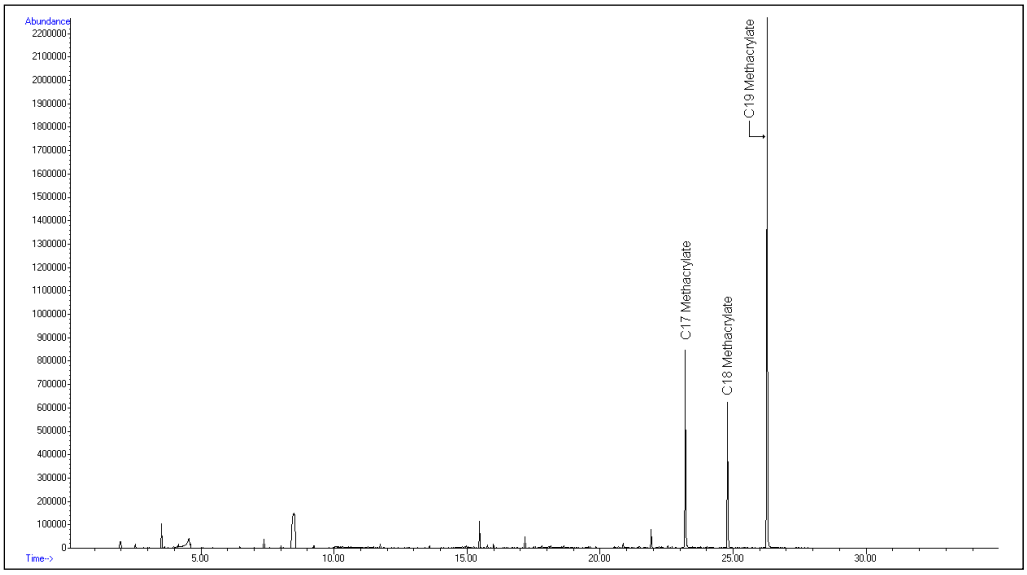

Figure 15: SIM of Substitute C6 Fluoropolymer showing Multiple Methacrylate Peaks

Conclusions

Both FT-IR and pyrolysis-GC/MS have important niches to fill in an analytical or quality control laboratory. FT-IR is cheap, fast and provides useful chemical information about the entire structure of a sample. Pyrolysis-GC/MS isn't cheap or fast, and it requires good, basic background knowledge of chemical structure and bonding behavior in order to interpret the results. But pyrolysis-GC/MS provides information that is irreplaceable when troubleshooting quality control issues or when screening replacements for raw materials.

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