

LAB CONNECTIONS

LC-TRANSFORM®

INTERFACING CHROMATOGRAPHY WITH SPECTROSCOPY

AN-32 Determining Component Distributions in Paints and Coatings

The compositional analysis of coatings products poses a formidable challenge to the coatings chemist. A typical coatings formulation consists of a multi-component polymer base, vehicles that will be incorporated into the dried or cured coating, pigments, fillers, catalysts, and various additives. During the polymerization phase of manufacture comonomers and adducts are taken up to varying extent in the polymer mass. It is desirable to be able to determine the degree of incorporation of these components into the polymer mass, and the levels of residual monomers/oligomers that may remain at the completion of the polymerization process.

As an example, the amount and type of dispersant used in an emulsion polymerization has a profound effect on the extent of inclusion of oils into the polymer synthesis mass. A technique for mapping the composition distribution across the molecular weight range of the coating can enable the formulator to optimize the finish properties of the product.



THE COATINGS PROGRAM MODULE

Lab Connections provides software (*3D/IR*) for analysis of polymers by GPC-FTIR, and makes available a number of application notes describing the techniques of polymer analysis. The application notes AN-3, AN-6, AN-10, AN-15, AN-16, AN-21, AN-22, AN-25, and AN-27 all deal with polymer analysis. Recently we have developed a specialized add-on to *3D/IR*, providing capabilities for the analysis of coatings formulations. This add-on has been designed as a rapid analytical tool for the coatings product development environment. While spectral interpretation skills are required for initial setup of a new formulation, day-to-day analysis of similar samples is automated, and does not require the user to be skilled in infrared spectral interpretation. (Lab Connections can provide assistance in method development for those unfamiliar with FTIR spectral interpretation.) Standardized graphical and tabular results can be viewed on the computer screen, or printed as hard copy for reports.

In brief, the analyst performs the following steps:

- Synthesize a coatings formulation
- Separate a coatings formulation by Gel Permeation Chromatography, and collect the components using the LC-Transform.
- Obtain the spectral data set from the LC-Transform collection.
- Load the data set into 3D/IR. Also input the bulk amounts of the polymer constituents in the formulation.
- Invoke the Coatings Program Module to obtain quantitative components distribution

ANALYSIS OF AN EXPERIMENTAL ACRYLIC WATER-BASED FINISH

An acrylic formulation was prepared by emulsion polymerization. The formulation included acrylic and styrene monomers, as well as adducts that would be included into the cured finish.

Table 1: Components

COMPONENT	SPECTRAL IDENTIFICATION BAND	% NON-VOLATILES
styrene	700 cm ⁻¹	38.2%
acrylic acid	1700 cm ⁻¹	4.6 %
acrylate	1740 cm ⁻¹	23.1%
adducts	1740 cm ⁻¹	34%

The system was emulsion polymerized, and the resulting reaction mass was taken up in tetrahydrofuran (THF). 100 ml of a 0.2% (wt/vol) solution was injected onto a set of size exclusion columns.

The LC-Transform sample collection was done on a 1-TIME™ porous polyethylene membrane disc. Since the formulation contains relatively low viscosity ingredients, the membrane disc is used to prevent lateral spreading under nozzle deposition conditions. LC-Transform collection and processing conditions are listed below:

Table 2: Experimental Conditions

EXPERIMENTAL CONDITIONS	
Column set	Waters Styragel 10-4th and 10-3rd, 10 microns, 300mm X 7.8mm. 35 deg C.
Mobile phase	THF: 1.0 ml/min
LC-transform collection medium	Polyethylene 1-Time disc

FTIR

36 scans/spectrum, 4 cm⁻¹ resolution

Figure 1 shows a three dimensional view of the time arrayed FTIR spectra of the deposited chromatogram. In this figure the earliest eluting (highest molecular weight) are in the foreground. For the elution time between 10 and 20 minutes the deposit is polymeric. The non-polymeric components are seen in the 20 -25 minute range.

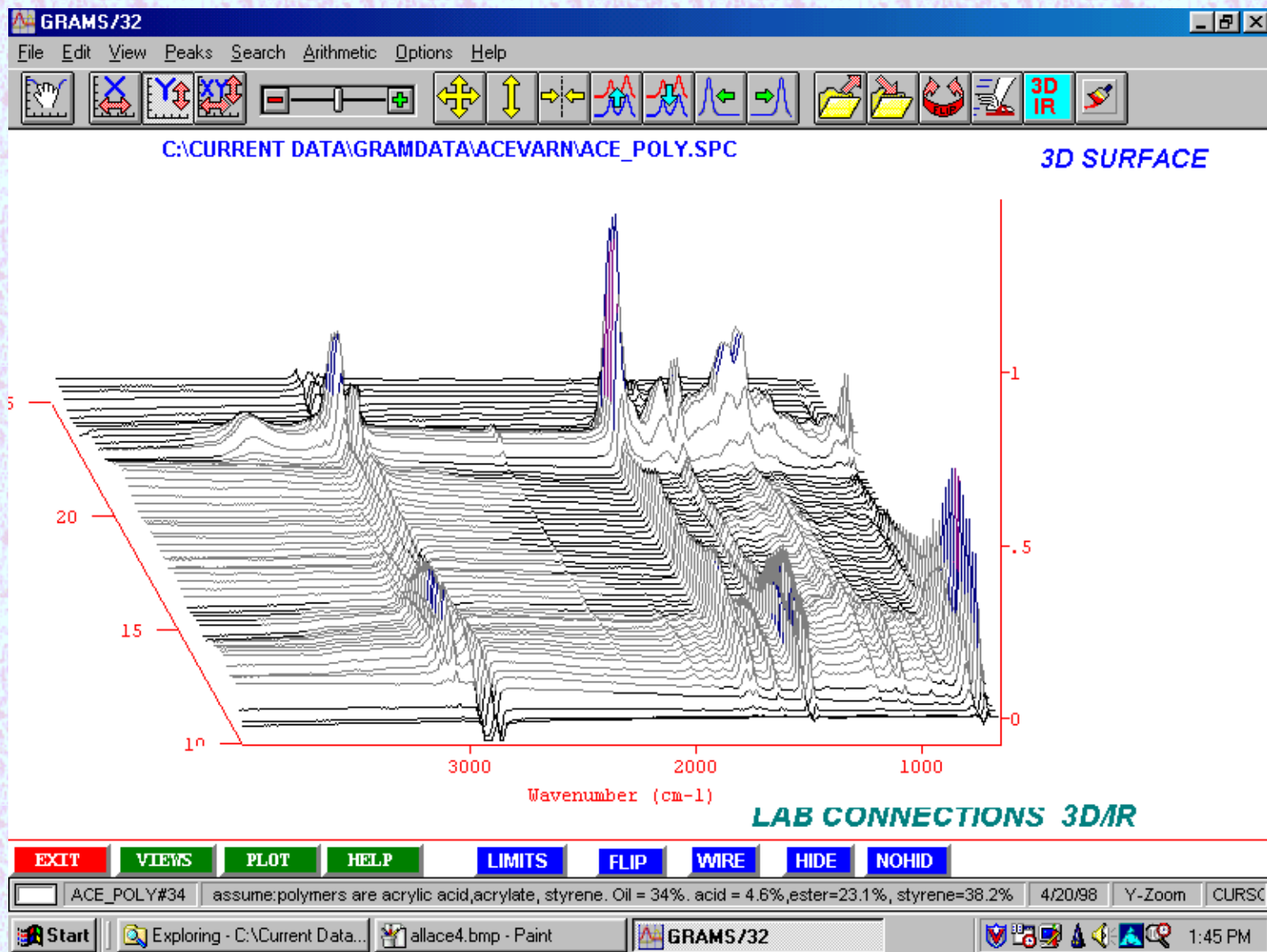


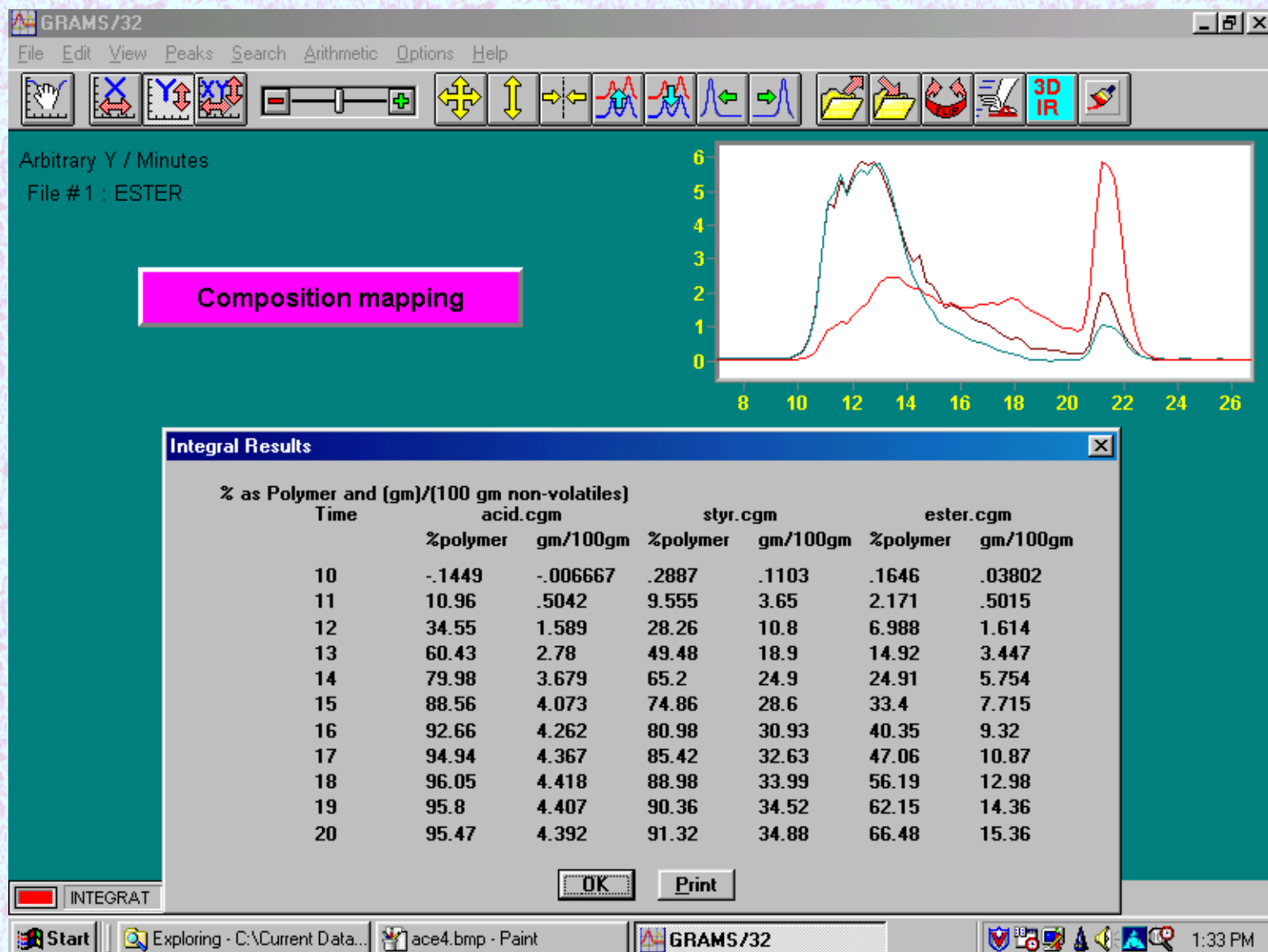
Figure 1.

Each of the polymer components gives rise to unique spectral bands. For instance, styrene has a strong band at 700 cm⁻¹, and a plot of this band intensity with time provides a chromatogram for the styrene content.

Using the Coatings Program Module the user selects the bands representing specific components, specifying parameters such as left and right edges of the band, peak height or area, etc. These are input to the program as a METHOD. Each time a new sample is processed, these selected methods will automatically generate the functional group chromatograms as defined by these methods. Using the formulation bulk composition

information (as shown in table 1), the program re-scales the chromatograms such that the total area under each chromatogram equals the total bulk amount of the corresponding component.

The upper right portion of Figure 2 shows the display presented derived from the data in Table 1 is input to the program. At the upper left the functional group chromatograms of the polymer components are displayed. They can either be displayed full scale as shown here, or scaled to their actual mass amounts. The table in the lower center of the screen shows the amount of each component eluted as a function of elution time. Monomeric components began to elute at 20+ minutes. It is apparent that polymerization was not 100% complete, for the co-monomers, as monomer or low molecular weight oligomers are evident in the 20 - 24 min elution time frame. In the case of the ester chromatogram, part of this region also includes adducts which have ester groups.



This screen then tabulates the degree of incorporation of components into the polymer mass, and the relative molecular weight distribution of the components. Changes in the synthesis process will reveal the composition distribution of components.

Figure 2.

Note the button labeled **Composition mapping**. Clicking on this button invokes a screen designed to show the relative percentage composition of components as a function of elution time. Figures 3 and 4 show the displays for the styrene and ester co-monomers. There are two traces shown in each figure. The trace common to both figures 3 and 4 represents the total polymer mass distribution. The negative sloping trace in figure 3 is the %styrene concentration of the polymer, while the upward sloping trace in figure 4 represents the ester concentration of the polymer. They show that the co-polymerization is skewed. The earliest eluting (highest molecular weight) polymer is approximately 80% styrene co-monomer. With continuing elution time (lower mol wt) the styrene content drops, and the ester content increases.

Thus, one measures not only the amount of monomer inclusion into the polymer mass, but also the composition variation dictated by the reaction kinetics.

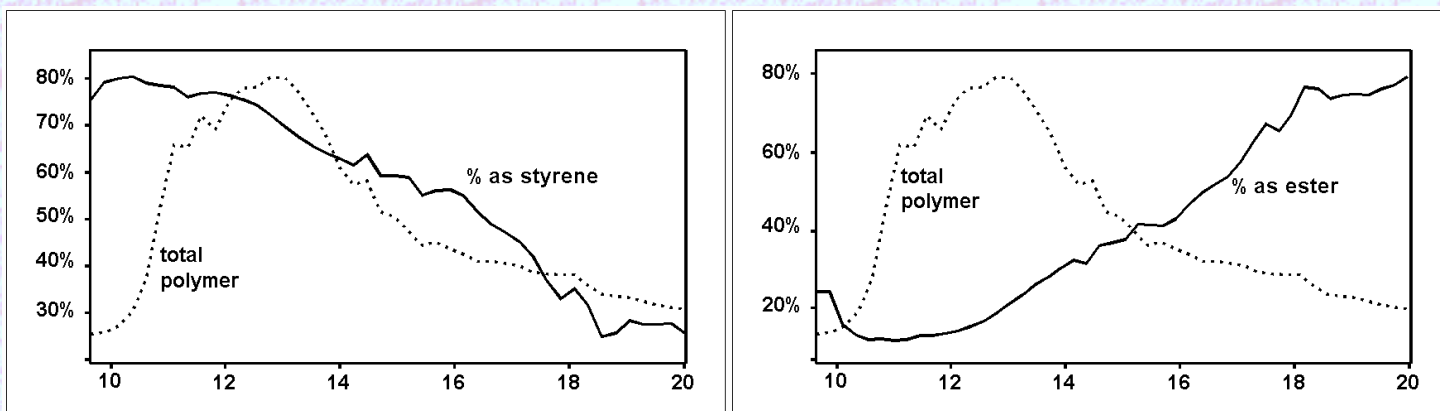


Figure 3. Figure 4.

CONCLUSION

The characterization of coatings formulations poses a major challenge to the analyst. Starting components may be completely or partially incorporated into the polymeric fraction of the reaction product. Co-monomers are seldom uniformly incorporated. The use of GPC-FTIR makes it practical to routinely characterize reaction products, and to correlate this compositional analysis with observed physical-chemical properties of the formulation.

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