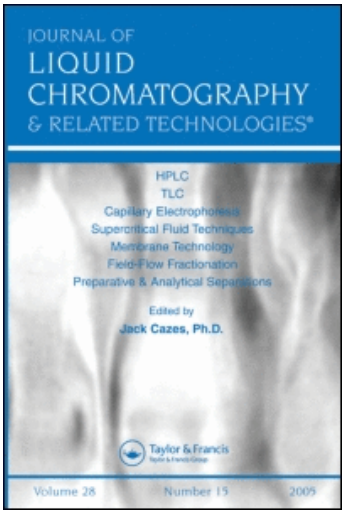

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USE OF GEL PERMEATION CHROMATOGRAPHY IN THE CRIME LABORATORY

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ABSTRACT

In this study, the ways in which GPC can be integrated into the crime laboratory's present analytical scheme for polymer products will be examined. Fingerprint chromatograms and chromatograms illustrating molecular weight determination of two types of commonly encountered physical evidence (fibers and tail light lense fragments) will be compared and discussed. The techniques involved in sample preparation and data interpretation will be given. Finally the potential advantages of GPC for use in the crime laboratory will be presented.

INTRODUCTION

When studying a polymer, polymer scientists routinely use GPC (gel permeation chromatography) to estimate the molecular weight and the molecular weight distribution of the polymer in question. In fact, GPC has become the method of choice in numerous cases for measuring these polymer properties. Current literature contains detailed descriptions of this type of application (1,3). GPC has also found extensive use as a quality control technique for monitoring a wide variety of parameters related to the manufacture of finished polymer products. GPC has been used to monitor parameters such as the

variation in molecular weight of polymer during a production run, and variations in concentration of polymer, dye or colorant, antioxidant and plasticizer as they relate to a "good" or "bad" finished polymer product (2,3,4,5).

These applications of GPC should be of particular interest to criminalists because a wide variety of polymer products are routinely encountered in the trace evidence section of a crime laboratory. Such items as synthetic fibers; tape - in the form of first aid, wrapping, masking or electrical tape; film wrapping materials or bags; paint and paint chips; grease and oil; rubber or rubber-like products; and automative parts such as bumpers, grills, tail-light lenses, and window and door moldings are just a few of the types of polymer products found in case work associated with suspect criminal actions. For the criminalist, analysis of this type of trace evidence can be frustrating because many of the items encountered are mass produced and, as such, tend to be nearly homogeneous in composition within a given "batch" of product. To complicate the situation, suitable manufacturer reference standards normally are not available. Perhaps the most difficult problem the criminalist faces is one related to the origin of the particular polymer product under examination. The question the criminalist must answer is, "to what extent" do the properties of the questioned fiber sample found (for example) in the suspect's car match those collected from the victim's clothing?

Comparative analyses required to answer this question can be very time-consuming, because they usually involve collecting data from a wide variety of chemical and instrumental sources. Once the data concerning the particular type of physical evidence has been collected, the criminalist must sit down and interpret it. The success or failure of this interpretation rests, in many instances, upon the range and variety of

data collected and the experience of the criminalist in working with this type of physical evidence. Both aspects of the analysis are necessary for a successful interpretation.

In this study, we will examine the ways in which GPC can be integrated into the crime laboratory's present analytical scheme for polymer products. "Fingerprint" chromatograms and chromatograms illustrating molecular weight determinations from two types of commonly encountered physical evidence (fibers and tail-light lense fragments) will be compared and discussed. The technique involved in sample preparation and data interpretation will be given. Finally, the potential advantages of GPC for use in the crime laboratory will be presented.

EXPERIMENTAL

1. Polymer Samples

A. Fiber Samples

Samples of acetate, polyamide, and acrylic fibers were selected at random from cloth samples available from local fabric shops. Two samples of blue acetate fibers were chosen specifically for their similarities in appearance and optical properties. Additional samples of one type of acetate fiber were obtained from a single bolt of material over a period of three months.

B. Tail Light Lenses

Two hundred fragments from turn signal and tail light lenses were collected at random from cars found at a local junk yard. Every effort was made to record make, model, and year of the car from which the lense fragment was collected; however, in some instances, the extent of damage or decay of the car body prevented accurate identification. Red, yellow and clear (white) lenses were collected.

2. Sample Preparation

Sample size was chosen in such a fashion as to be consistent with the size of trace evidence samples normally encountered in the crime laboratory and consistent with the size of sample used in GPC analyses. Sample concentration ranged from 0.25-0.50% (i.e., 5-10 mg/2.00 ml) in all cases in this study. Size of sample injected ranged from 20 to 100 µl depending upon the particular polymer product under examination. All samples were dissolved in an appropriate solvent, filtered (0.45 µm filter), and analyzed as soon as possible generally within 2 hours. Inconsistent results were obtained if the dissolved polymer samples were allowed to sit for more than one day between analyses. Every attempt was made to dissolve the sample in THF (tetrahydrofuran). THF was used to dissolve acetate fiber and tail light samples; dimethylformamide and hexafluoroisopropanol were used to dissolve acrylic and polyamide samples respectively.

3. Solvents/Flow Rate

Tetrahydrofuran (Burdick and Jackson), 2.0 ml/min., was used as the mobile phase in this study.

4. Columns

All columns used in this study were µStyragel GPC columns obtained from Waters Associates, Milford, Massachusetts.

A. "High Bank": Exclusion Limits: 10^6, 10^5, 10^4, 10^3 & 500Å (nominal)

B. "Low Bank": Exclusion Limits: 10^3, 2 x 500, & 100Å (nominal)

C. "Quick Screen": Exclusion Limits: 2 x 100Å (nominal)

Each bank of columns was calibrated using high purity hydrocarbons (for the low molecular weights) or narrow range polystyrene calibration standards (high molecular weights). Polystyrene standards were obtained from Waters Associates, Milford, Massachusetts.

5. Equipment

Waters Associates Model 244 Liquid Chromatograph consisting of a U6K Injector, Model 6000A pump, Model 440 UV detector (254nm), and Model 401 Refractive Index Detector.

Recorder: Texas Instruments Servo Riter II (dual pen).

RESULTS

1. "Fingerprint" Chromatogram Comparisons

Samples of acetate, polyamide, and acrylic fibers were prepared and chromatographed on three banks of columns. An illustration of the type of data obtained in this study for the fibers, one that should be of particular interest to the criminalist is shown in Figure 1. The two chromatogram were produced from two blue acetate fibers (terry and taffeta) which had remarkably similar optical properties. Fibers, when separated from each material, "looked" nearly identical in color, color density, and diameter. This remarkable similarity was confirmed by immersing the fibers in refractive index liquid $n_D^{25} = 1.476$. The inherent contrast of the fibers and the contrast of the Becke line in this liquid were very similar. When viewed under crossed polars with a red plate, the fibers showed almost indistinguishable interference colors. At this point, and without further testing, the criminalist might be tempted to make a statement concerning the similarity of the two fiber samples. When viewed in a "fingerprint" comparative nature, however, the GPC chromatograms in Figure 1 show distinct differences in the dye (small molecule-low molecular weight) region of the GPC chromatogram. This difference was confirmed by collecting this fraction of the sample and scanning the visible spectrum on a recording spectrophotometer. Figure 2 reinforces (with visible spectra) the differences between the samples which were originally detected in the GPC chromatograms. The GPC chromato-

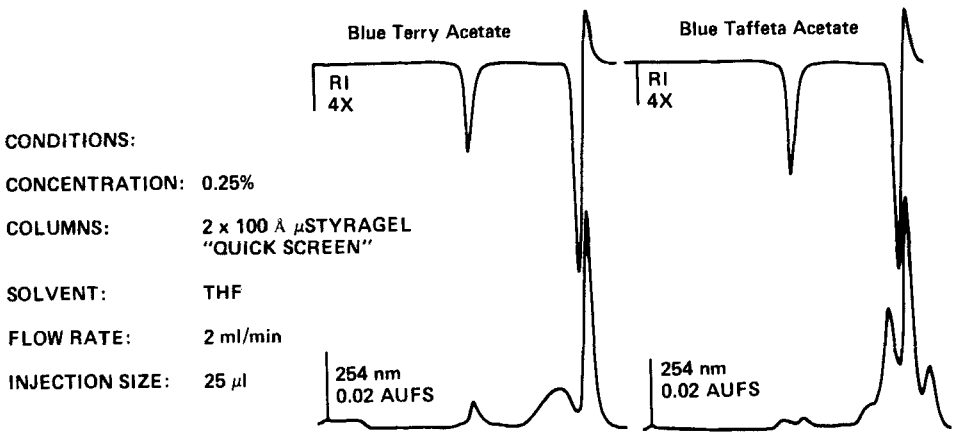

FIGURE 1

QUICK SCREEN CHROMATOGRAM OF BLUE ACETATE: "FINGERPRINT COMPARISON"

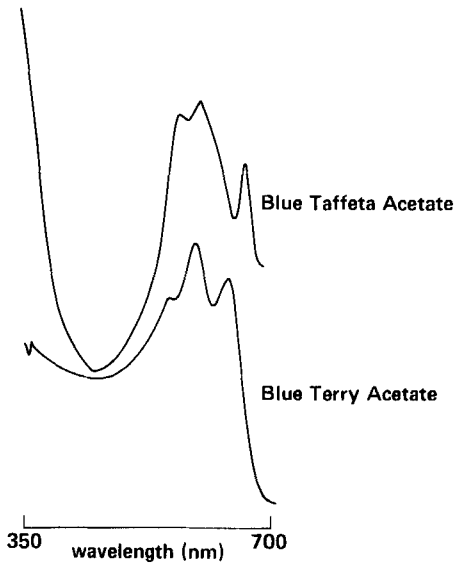

FIGURE 2

DYE FRACTION COLLECTED FROM BLUE ACETATE FIBERS: VISIBLE SPECTRA

grams of the acetate fibers analyzed with the three banks of columns did not reveal significant differences in polymer molecular weight or molecular weight distribution. This similarity in polymer composition was further confirmed by collecting the polymer fraction (high molecular weight) of the sample, pyrolyzing it, and comparing pyrolysis gas chromatograms. The pyrolysis chromatograms obtained for the two acetate fibers are shown in Figure 3. GPC chromatograms for 40 different acetate, polyamide, and acrylic fibers were obtained using all three banks of columns.

2. Molecular Weight Determinations

Solutions of red, yellow and clear tail light and turn signal lenses were prepared and chromatographed on the three banks of columns. Figure 4 shows a "fingerprint" comparison of GPC chromatograms from six randomly selected red tail light lenses.

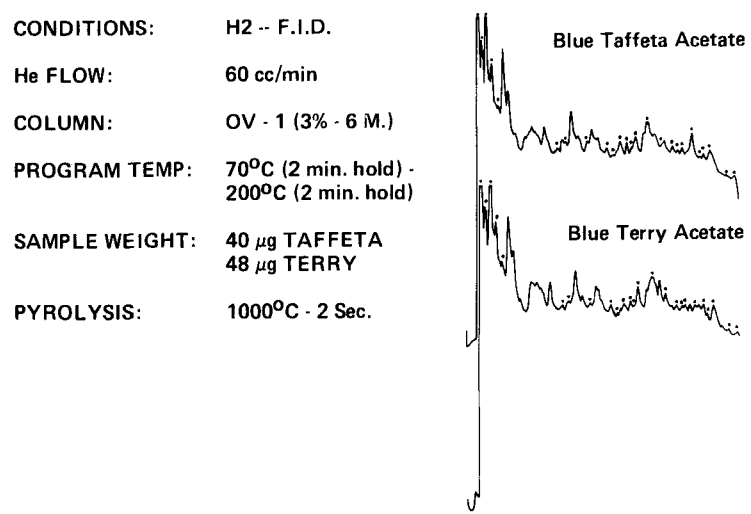

FIGURE 3

PYROLYSIS G.C.: POLYMER FRACTION COLLECTED FROM BLUE ACETATE FIBERS

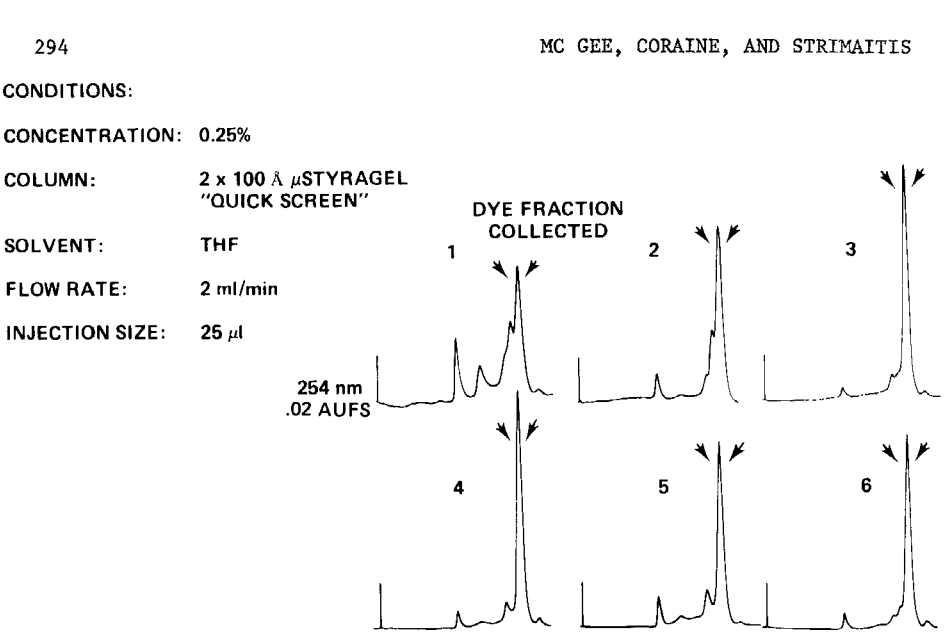

FIGURE 4

QUICK SCREEN CHROMATOGRAM OF RED TAIL LIGHT LENSES

The apparent similarity in the low molecular weight dye fractions was reinforced by collecting this fraction of the sample (as indicated in Figure 4) and scanning the visible spectrum on a recording spectrophotometer. However, the variations in peak height ratios of the higher molecular weight components provided a basis for discriminating between the samples. Visible spectra for two tail light lenses are shown in Figure 5. Variations in the molecular weight of the polymer in the tail light lense fragments were detected using the "High" bank of columns. The "molecular weight" chromatograms for the six fragments are shown in Figure 6. A molecular weight scale is superimposed above the peaks in Figure 6. The differences in molecular weights for polymer samples shown in Figure 6 were not detected in the IR spectra of the polymer fractions collected from the six GPC runs. The six

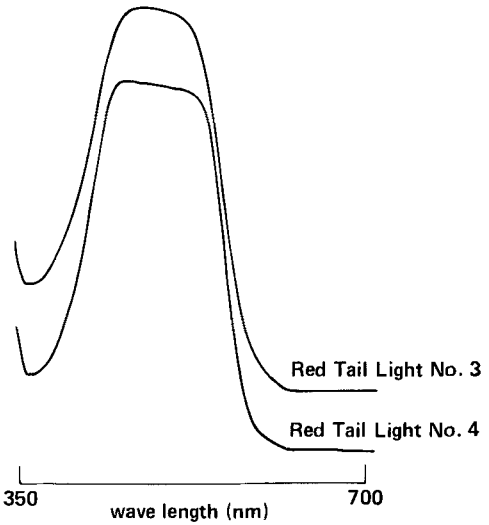

FIGURE 5

DYE FRACTION COLLECTED FROM RED TAIL LIGHT LENSES: VISIBLE SPECTRA

CONDITIONS:	
CONCENTRATION:	0.25%
COLUMNS:	"Hi Bank" (10^6, 10^5, 10^4, 10^3, 500 Å, μSTYRAGEL)
SOLVENT:	THF
FLOW RATE:	2 ml/min
DETECTION:	4X RI
INJECTION SIZE:	200 μl

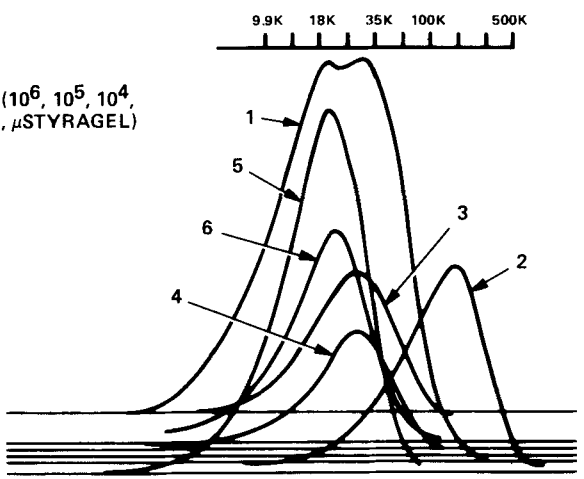

FIGURE 6

MOLECULAR WEIGHT DETERMINATION: POLYMERS OF SIX RED TAIL LIGHT LENSES

GPC chromatograms shown in Figure 6 are representative of those from the 200 tail light fragments analyzed.

DISCUSSION

When considering the integration of GPC into existing crime laboratory procedures for polymer products, the criminalist should first become fimiliar with the basic principles of GPC, interpretation of chromatograms and generation of molecular weight data, and sample handling techniques. Since most criminalists will use the technique in a comparative way, (i.e., by comparing GPC chromatograms of questioned and known samples) in order to make statements concerning the origin of the samples, the criminalist must have knowledge of and confidence in the operation of the GPC system.

One way to gain this confidence is by calibrating all banks of columns using narrow range calibration standards according to established procedures (3,4,5,6,7). Once calibrated, the columns should be tested regularly using fresh calibration standards to assure reproducible performance. Calibration will also familiarize the criminalist with the molecular weight performance range of each bank of columns. For example, in this study, the "high" bank was found to cover a molecular weight range of about 100 to 1,000,000 and was best suited to resolving most components in a finished polymer product. The "low" bank of columns covered a narrow molecular weight range of molecules (100 to about 1,000) but with better resolution of peaks. This bank of columns was best suited to resolving components in the dye-additive package of the finished polymer product. It should be noted that GPC chromatograms recorded using the "high" and "low" banks will be at least 30 minutes long. The "quick-screen" bank of columns provides adequate separation between large and small molecules and no more than approximately six minutes are required to record a chromatogram. Recalling the fingerprint comparison between the blue fibers, in this illus-

tration, enough information was available from the chromatogram to indicate a difference in the dye package for the two fiber samples.

Periodic recalibration is essential for making comparisons of polymer samples over an extended period of time. In this study, the relative composition of polymer-dyes-additives in one acetate fabric was monitored over the length of one bolt of material. Samples cut from one bolt were purchased over a three month time period and analyzed. No significant variations in composition of polymer-dyes-additives or molecular weight parameters of the polymer was detected within this time frame.

Calibration also provides the criminalist with an estimate of a number of molecular weight related parameters for the polymer in question. The number average molecular weight ($\bar{M}_n$), weight average molecular weight ($\bar{M}_w$), and heterogeneity factor ($\bar{M}_w/\bar{M}_n$) can, and in some instances, should be calculated in order to characterize the polymer in question. The heterogeneity factor describes the broadness of the molecular weight distribution. Such characteristic information might prove useful to the criminalist when attempting to make a comparison between two very similar looking (GPC chromatogram-wise) polymer samples (3,4,5). Calculations are straightforward and computer programs are available to minimize the time required to perform them (3,6,8).

In addition to calibrating the columns, the criminalist should become familiar with the current state of art concerning the effects of sample size, flow rate, recorder accuracy, column arrangement, temperature, and aging of columns on the GPC chromatograms and the subsequent interpretation and comparison of data (2-5, 7-14).

This discussion of column calibration and GPC operating parameters should not discourage the criminalist from intergrating GPC into existing crime lab polymer analysis procedures. GPC is a direct and straightforward technique to learn and to use. Column selection and sample pre-

paration are not complicated (15). Once proper precautions have been taken, comparison of fingerprint GPC chromatograms is direct. Most polymer scientists use the refractive index detector for their polymer studies. Since the criminalist is interested in all aspects of the polymer-dye-additive package in the finished polymer product, data from UV and fluorescent detectors should be used in making comparisons of questioned samples. Unlike the polymer scientist, the criminalist normally has limited sample with which to work. When using GPC in the crime lab, the entire sample or specific components of the sample may be collected and used for other analytical or instrumental techniques. GPC is a sensitive technique. Sensitivity is a function of sample concentration, detector type, and the mobile phase. In general, sensitivity of GPC is suited to the size and/or quantity of the sample encountered in the crime lab. Due to the mechanism of GPC, the technique is very predictable; a GPC analysis has a definite beginning (V_o) and end (V_t). And, by suitable calibration, various molecular size species will elute at predictable locations in the chromatogram. Finally, GPC provides information (i.e. molecular weight parameters) about the polymer sample under examination that is not accessible through use of other chromatographic techniques.

In conclusion, it is hoped that the results of this study and the subsequent discussion will encourage criminalists to consider the integration of GPC into their analytical procedures for polymer products.

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