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The Analysis of Polyvinylchloride Wire Insulation by Gel Permeation Chromatography

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ABSTRACT: Polyvinylchloride (PVC) insulated stereo speaker wire from a homicide case involving the strangulation of a child was received by the FBI Laboratory for analysis. A method utilizing gel permeation chromatography to analyze PVC wire insulation was developed which was capable of discriminating between different commercially available brands of wire insulation. Using this method, we were able not only to link the wire found at the crime scene with a source from a suspect's residence, but also to associate it with a particular commercial brand of wire. The analysis of this case sample and other brands of stereo speaker wire is described.

KEYWORDS: criminalistics, polyvinylchloride, chromatographic analysis, gel permeation chromatography, polymer analysis, wire insulation

In the summer of 1983, a young boy was found strangled in a wooded area. Next to the body a piece of stereo speaker wire approximately 0.9 m (3 ft) long, believed to be the murder weapon, was found. Shortly after the discovery of the victim, a suspect was developed. A search of his residence revealed two different sources of stereo speaker wire.

The wire from the crime scene, along with wire from both sources of the suspect's residence, was submitted to the FBI Laboratory for analysis. The Laboratory was requested to determine if the wire found at the crime scene matched one or both sources of wire from the suspect's residence.

During the initial physical examination, no visible differences could be detected between the wires. Both samples, shown in Fig. 1, were dual-conductor copper wire insulated with clear polyvinylchloride (PVC), as determined by infrared spectroscopy. A sample of the wire insulation was analyzed by pyrolysis gas chromatography, a routine technique used in forensic science laboratories for polymer analysis. This method did not reveal any significant differences between the wire from the suspect's home and that from the crime scene. However, analysis of clear PVC insulation from several other brands of wire using this method also yielded no significant differences between any of the insulation samples. Therefore, an alter-

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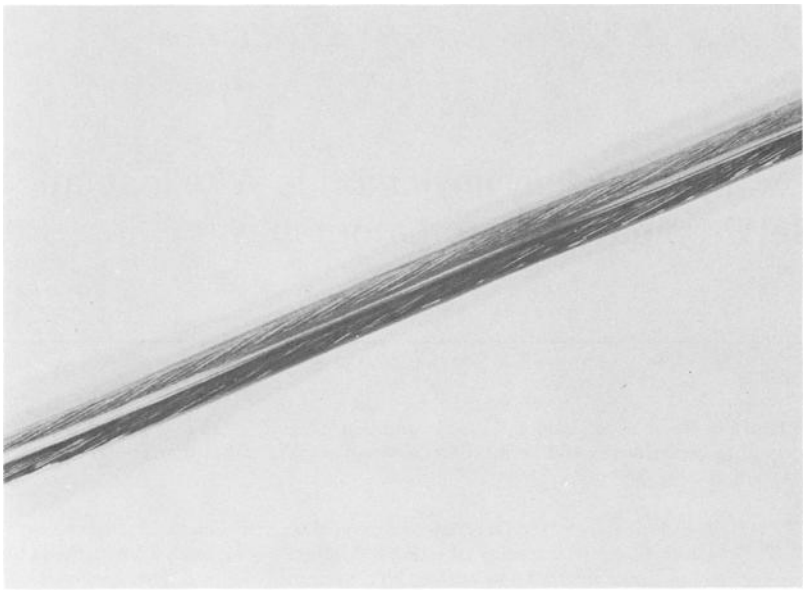

FIG. 1—*A sample of the polyvinylchloride insulated stereo speaker wire found at the crime scene.*

native method capable of discriminating between polymer samples of similar composition was sought.

Gel permeation chromatography (GPC), a technique new to forensic science for polymer analysis, was being explored by the FBI's Forensic Science Research Group. GPC is commonly used in industry to characterize polymers by their molecular weight distribution [*1-3*]. It was determined that GPC could offer the discrimination necessary to distinguish between different brands of PVC wire insulation.

GPC, also referred to as size exclusion chromatography, is a form of liquid chromatography where molecules are physically sorted according to their effective size in solution (hydrodynamic volume). Because a polymer is composed of similar molecules of differing sizes and molecular weights, no one number can be assigned to a polymer to describe its molecular weight accurately. Thus, the molecular weight distribution of a polymer is expressed by molecular weight averages. These averages are calculated based on a calibration curve prepared with known molecular weight standards.

The GPC chromatograms relate to information about the physical properties of the polymer (for example, brittleness and tensile strength) and the lower molecular weight additives. These additives (for example, plasticizers, antioxidants, and dyes) are compounds added by the manufacturer to give specific desired characteristics to the product [*4-6*]. GPC has been used to characterize such polymers as adhesives [*7-11*], polymethylmethacrylates such as taillight lenses [*12-13*], plastic tapes [*13*], paints [*14,15*], fibers [*16*], and petroleum products [*13,17-19*]. Based on its widespread applications and demonstrated discriminating ability, it was felt that GPC offered the most useful information of any of the previously used techniques in this case.

Experimental Procedure

The Waters Model 150 C Gel Permeation Chromatograph (Waters Associates, Milford, MA) equipped with an autosampler and a Model 401 differential refractometer was used for

all analyses. Detector response was measured as the difference between the refractive index of the mobile phase and that of the sample dissolved in the mobile phase. Three Ultrastyragel columns (Waters Associates, Milford MA) having pore sizes of 10^4, 50 and 10 nm (10^5, 500, and 100 Å), respectively, were used in series. The mobile phase for all analyses was HPLC grade tetrahydrofuran (Burdick and Jackson, Muskegon, MI) at a flow rate of 1.5 mL/min. All experiments were performed at 35°C to enhance efficiency of the columns by lowering viscosity.

To prepare a calibration curve for subsequent molecular weight determinations, twelve narrowly dispersed polystyrene standards (Supelco, Bellefonte, PA) were analyzed at the conditions described above. Data were collected on a Waters Model 730 Data Module. A calibration curve based on peak retention time versus log molecular weight was prepared and stored by the data module in the form of a third-order plot. The calculated correlation coefficient was 0.9998.

The insulation from wire recovered from the residence and the crime scene, along with several other commercially available brands of stereo speaker wire, was analyzed at the conditions described above. Two samplings from each specimen were taken and each of these sample solutions was run in duplicate (two injections from each vial). All samples and standards were prepared as 0.1% solutions in tetrahydrofuran (THF) and were allowed to sit at 35°C for at least 1 h, but no longer than 3 h, with gentle mixing to allow the polymer to dissolve and disperse. Shaking of the samples was avoided because of possible "shearing" of the high molecular weight molecules [*20*]. All samples were filtered through 0.5-μm Millex SR membranes (Waters Associates) to remove any insoluble particles or contaminants which could interfere with the analyses.

Results and Discussion

Figure 2 illustrates chromatograms of the insulation from the wire found at the crime scene and that found in the suspect's residence. The chromatograms show the molecular weight distribution of the PVC polymer and a baseline separation of the monodisperse addi-

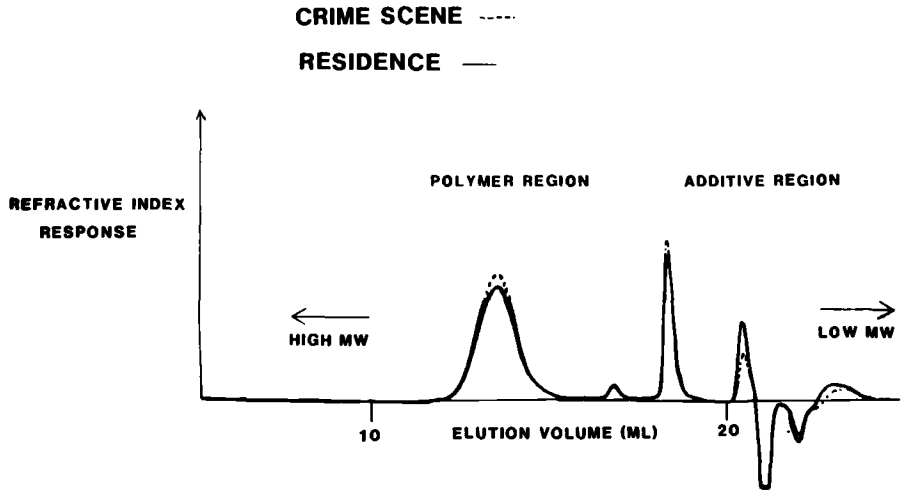

FIG. 2—*A comparison of GPC chromatograms of PVC insulation from wire found at the crime scene and in the residence of the suspect. The molecular weight distribution is shown as the polymer region, with the lower molecular weight additives eluting later. The samples contain the same molecular weight distribution and additives in the same relative concentrations.*

tives. Both regions compared favorably in both specimens, indicating the same molecular weight distribution and corresponding additives in the same relative concentrations. In addition, the chromatograms from the two different sources in the suspect's residence were indistinguishable from each other.

To determine the significance of the results, several similar commercially available specimens of stereo speaker wire with clear PVC insulation were examined using this method. Figures 3 to 6 illustrate chromatograms of some of these commercial products compared to the crime scene specimen.

Figure 3 shows a comparison of the questioned wire insulation from the crime scene with the commercial product Saxton wire (Congers, NY). The shape of the polymer region in the

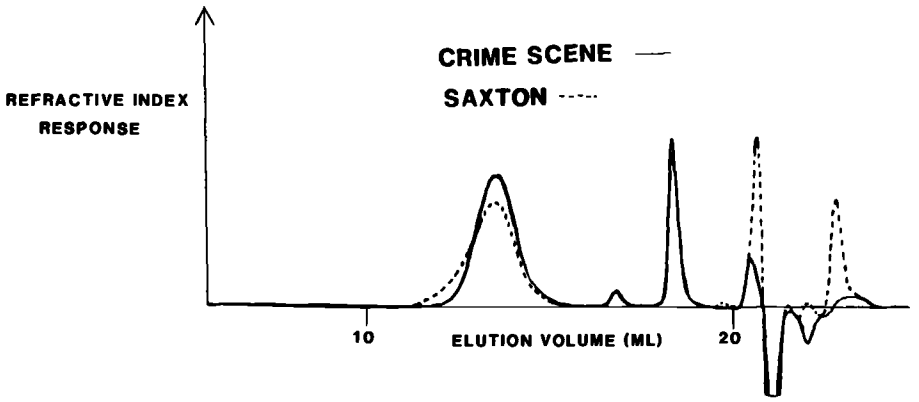

FIG. 3—*A comparison of GPC chromatograms of PVC insulation from wire found at the crime scene with that from the commercial product Saxton wire. The molecular weight distributions are different in shape and elution time, with the Saxton wire possessing a higher molecular weight distribution. In addition, some of the additives differ in relative concentrations.*

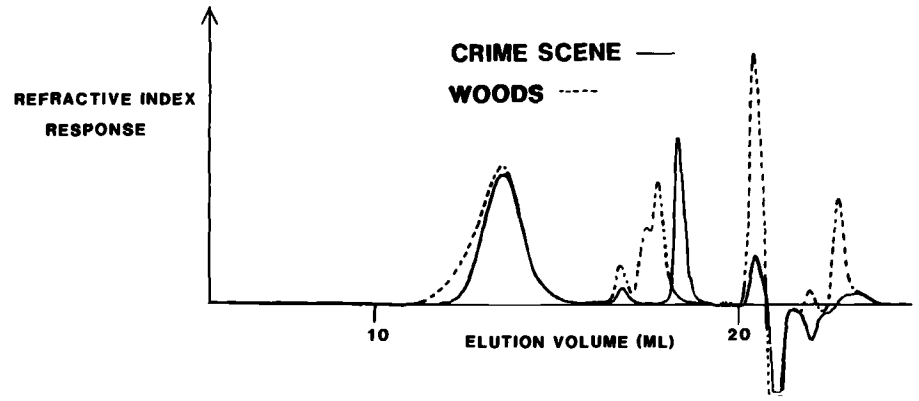

FIG. 4—*A comparison of GPC chromatograms of PVC insulation from wire found at the crime scene with that from the commercial product Woods wire. The Woods sample represents a much higher molecular weight distribution and contains several additives either not present in the crime scene sample or present in different relative concentrations. The two samples are clearly different both in the polymer region and in the additive region.*

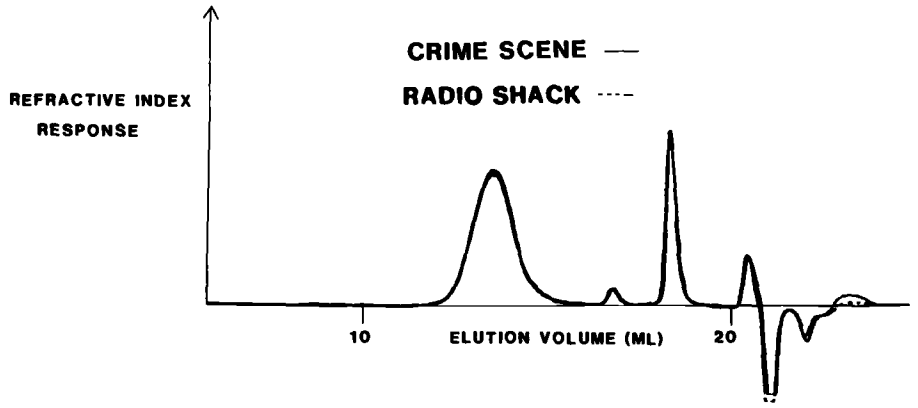

FIG. 5—*A comparison of GPC chromatograms of PVC insulation from wire found at the crime scene with that from the commercial product Radio Shack speaker wire. The molecular weight distributions are indistinguishable and the two samples contain the same additives in the same relative concentrations.*

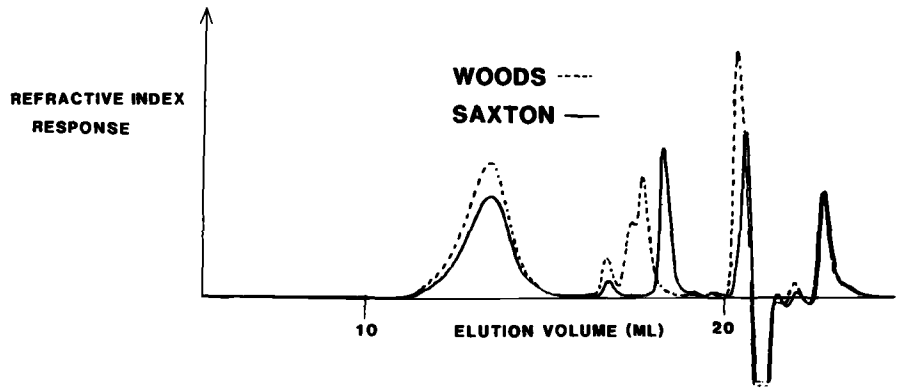

FIG. 6—*A comparison of GPC chromatograms of PVC insulation from the commercial products Woods and Saxton wire. Although they were analyzed at slightly different concentrations, the shape and elution time of the molecular weight curves are the same, reflected by their molecular weight averages (Table 1). The additives in these two samples, however, are quite different. With samples such as these where one cannot distinguish between their molecular weight distributions, one must rely on the additive profiles to discriminate between the samples.*

Saxton insulation is significantly different from that of the crime scene specimen, with a higher molecular weight distribution. Listed in Table 1 are the calculated molecular weight averages for some of the samples studied. As indicated, the weight-average molecular weight for the molecular weight distribution of the Saxton wire insulation was calculated by the data module to be 194 733 daltons, while that for the crime scene specimen was determined to be 133 387 daltons.

Reported error inherent to GPC weight calculations varies from 1 to 3% relative standard deviation, taking into account sample and instrument variation [*21-24*]. Repeated analysis of the same sample solution and analysis of different samples from the same specimen (for example, samples of the wire insulation taken along the length of the wire) indicated a standard deviation not exceeding 2% of the mean in all samples studied. The highest calculated

TABLE 1—*Calculated weight-average molecular weights for some of the samples of wire insulation studied, indicating the percent difference from the residence specimen. Repeated analysis of the same sample solution has indicated that up to a 2% relative standard deviation in calculated values of the sample can be expected.*

	Molecular Weight Average	Percent Difference From Residence
Residence	135 194	
Crime scene	133 387	1.3
Radio Shack	135 936	0.55
Saxton	194 733	44
Woods	194 824	44

coefficient of variation for a sample was 0.020 with $n = 10$. Thus, the 44% difference in molecular weight averages between the crime scene and the Saxton samples is highly significant ($p < 0.001$).

Although the additive profiles show some similarities (Additives 1 and 2 are present in the same relative concentrations), there are significant differences in the relative concentrations of Additives 3, 4, and 5.

A comparison of the questioned sample with the commercial product Woods wire (Carmel, IN; Fig. 4) again shows significant differences both in the polymer distribution (calculated values showed a difference of 44%), and in the additive profile. Several additives found in the Woods insulation are not present in the questioned sample. Where similarities do occur (Additives 1, 3, and 5), their relative concentrations are different.

Figure 5 is a comparison of Radio Shack brand speaker wire (Tandy Corporation, Fort Worth, TX) with the questioned sample. As shown, the molecular weight distributions of the two samples appear identical, as do the additive profiles. Additives 1 to 5 are present in both specimens in the same relative concentrations. The calculated molecular weight average of the questioned sample, shown in Table 1, is well within one relative standard deviation of the mean value established for Radio Shack brand wire insulation.

The Radio Shack wire insulation sample was purchased in Springfield, VA. To examine within-brand variation, other Radio Shack samples were analyzed, including one purchased in Dallas, TX, in 1978. These additional samples yielded chromatograms indistinguishable from that obtained from the initial sample purchased in Virginia in 1984. It was determined from a plant manager at Tandy Corporation that all Radio Shack speaker wire is produced in the same factory in Fort Worth, TX.

Based on these findings, it was concluded that the wire found at the crime scene could have been manufactured by Radio Shack. Law enforcement officials investigating the matter later confirmed that the wire found at the suspect's residence was, in fact, purchased at a Radio Shack outlet.

In the previous comparisons of different brands of wire with the questioned wire, there were significant differences in both the molecular weight distributions and in the additive profiles, with the exception of the Radio Shack brand. Sometimes, however, different brands of wire insulation were analyzed where calculated weight averages were in agreement, such as in the case of the Saxton and Woods wire, but where the additive profiles revealed major differences. This is illustrated in Fig. 6, with the calculated molecular weight averages appearing in Table 1. From these instances it was concluded that when determining the similarities of two chromatograms, one must visually compare (superimpose) both the molecular weight distribution and the additive profile in lieu of relying solely on calculated values of molecular weight averages [*25*].

Conclusion

In conclusion, it has been demonstrated that GPC can be a valuable tool in comparing polymer specimens such as PVC wire insulation. It was determined from this work that for this method of comparison to yield the most useful information, both the molecular weight distribution and the additive profile must be evaluated using the raw data chromatograms in addition to molecular weight averages. The method was highly discriminatory, evidenced by the fact that the crime scene specimen could be linked not only to sources in the subject's residence, but also to a particular brand of stereo speaker wire.

As a final note, the subject in this case pleaded guilty to committing a homicide using stereo speaker wire from his residence.

Acknowledgment

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