

# TECHNICAL NOTE

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## Pyrolysis Gas Chromatography of Automobile Rubber Bumper Guard Samples

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**REFERENCE:** Blackledge, R. D., "Pyrolysis Gas Chromatography of Automobile Rubber Bumper Guard Samples," *Journal of Forensic Sciences*, JFSCA, Vol. 26, No. 3, July 1981, pp. 557-559.

**ABSTRACT:** A piece from an automobile rubber bumper guard was found at the scene of a hit-and-run accident and was compared to a sample obtained from the front bumper guard of a suspect's vehicle. The samples were examined by the pyrolysis method of Chih-An Hu, which provides both a chromatogram of the volatile components and a pyrogram of the nonvolatile polymeric component.

**KEYWORDS:** criminalistics, rubber, automobiles

At the scene of a hit-and-run accident a strip approximately 25 by 6 mm (1 by 1/4 in.) of light-blue rubber-like material (Exhibit A) was recovered from the victim's vehicle, a 1973 Opel Rekord. Investigation led to a 1977 Plymouth, and a control sample (Exhibit B) was taken from the front rubber bumper guard.

Exhibits A and B were first examined by the nondestructive technique of attenuated total reflectance spectroscopy using a Fourier transform infrared spectrometer with data system [1]. Then portions of the samples were examined by synchronous excitation spectrofluorometry [2].

Hueske and Clodfelter [3] used gas-liquid chromatography to compare the thermal degradation products of rubber bumper guards from 19 different models of 1975 and 1976 American automobiles. The author has used their method with success but decided to try the method of Chih-An Hu [4] in an effort to obtain more information and greater reproducibility.

As pointed out by Chih-An Hu, "The pyrolysis chromatogram of a compounded polymeric material in its original form is not a simple pyrogram, but rather a compound one." As soon as the sample is placed in the hot injection port the more volatile components will be vaporized, producing a chromatogram. Then upon initial heating of the pyrolysis probe the remaining volatile components will be vaporized, producing a different chromatogram. Also, some of these vapors may undergo vapor phase pyrolysis, producing a pyrogram. Lastly, the polymer is pyrolyzed, producing another pyrogram. These steps all lead to a very complex pattern that is very hard to reproduce.

Chih-An Hu solved this problem by considering that a compounded polymeric material is composed of volatile and nonvolatile components. The injection port temperature is set so

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that most of the volatile components are vaporized when the probe is inserted. He found that 270°C was generally a good injection port temperature for rubbers. Upon insertion of the probe the chart paper is started and a temperature program begun, but no power is supplied to the pyrolysis probe. This method produces a chromatogram of the volatile components. Once this chromatogram is complete the probe remains in the injection port while the oven is cooled down. When the desired starting temperature is reached the sample is pyrolyzed, the chart paper again started, and another temperature program begun.

The results from one sample are a chromatogram of the volatile components and a pyrogram of the nonvolatile polymeric component; both of them are far more reproducible than the chromatograms superimposed on pyrograms obtained when pyrolysis is started as soon as the probe is placed in the injection port.

### Materials and Methods

The gas chromatograph was a Perkin-Elmer Model 3920B equipped with a flame ionization detector and a 1.8-m by 6.35-mm outside diameter glass column with 10% SE-30 on 60-80 mesh Chromosorb P, non-acid-washed.

Identical temperature programming conditions were used for both the chromatography of the volatile components and for the pyrolysis of the polymeric component. After an initial isothermal temperature of 100°C for 2 min, the temperature was raised by 16°C/min to 250°C and then held. The injection port and manifold temperatures were 270°C. The carrier gas was helium at a rate of 30 mL/min. For the chromatogram the chart speed was 5 mm/min, and for the pyrogram it was 10 mm/min. The attenuation for the chromatograms was  $10 \times 128$ , for the pyrograms,  $10 \times 64$ .

The pyrolysis unit was a Pyroprobe 190 made by Chemical Data Systems, Inc. The final pyrolysis temperature was 800°C with a 10-s interval and the ramp off. Sample size was between 1 and 2 mg. Samples were placed in quartz tubes, which were then inserted into the coil of the probe.

At the beginning of a run the normal septum cover was removed, the pyrolysis probe was installed, and the chart paper feed and the temperature program were immediately started. The length of time required to perform these tasks depends on one's dexterity, so retention times will vary slightly. However, the chromatogram patterns are quite reproducible.

Once the chromatogram of the volatile components was complete the oven temperature was recycled back to 100°C. The Perkin-Elmer Model 3920B gas chromatograph features an oven door that automatically raises and closes to assist in rapid cool down. The pyrogram runs were begun 5 min after the oven door had reclosed.

Figure 1 illustrates both the chromatograms (left side) and the pyrograms (right side) obtained with Exhibits A and B.

### Discussion

Although Chih-An Hu primarily developed this method for use in quality assurance work, it is equally applicable in forensic science comparisons. As illustrated in his article [4], several samples may give virtually identical pyrograms yet quite different chromatograms. This result indicates that although they all contain the same type of rubber, different solvents or methods were used in their formulation.

With the proper standards for comparison, it is possible to use the pyrogram to identify the type of polymeric material involved and therefore allow the forensic scientist to testify with more authority, for example, by identifying both samples as being butyl rubber rather than merely stating that the two produced matching patterns.

For hit-and-run cases, one could develop a data base (types of polymeric materials used in bumper guards for various makes, models, and years). Then when rubber bumper guard materials were recovered from an accident scene but no suspect vehicle had been located, the data base might help to narrow the search.

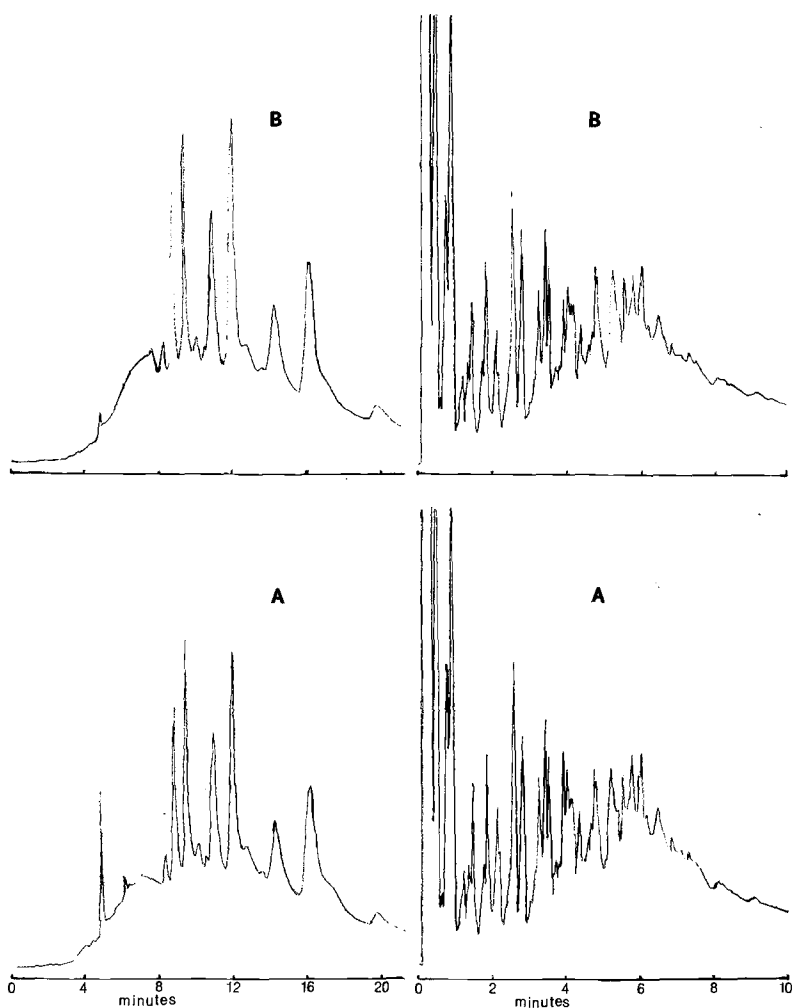


FIG. 1—Chromatograms (left) of the volatile components and pyrograms (right) from the non-volatile polymeric component of piece of rubber bumper guard material found at accident scene (A) and sample taken from suspect's vehicle (B).

## References

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