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Examination of Automobile Rubber Bumper Guards by Synchronous Excitation Spectrofluorometry

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ABSTRACT: Automobile rubber bumper guard material may be of evidentiary value in hit-and-run accident investigations. Fifty-six automobile rubber bumper guard samples were examined by synchronous excitation spectrofluorometry using a dichloromethane solvent. During sample preparation, additional discrimination was possible by observing the relative densities of the different samples in dichloromethane. The 16 samples that were not uniquely distinguished by this combination were further examined by gas-liquid chromatography.

KEY WORDS: criminalistics, automobiles, rubber, spectroscopic analysis

The technique of synchronous excitation spectrofluorometry (SES) was first introduced by Lloyd [1] in 1971. In the examination of complex mixtures of fluorescent compounds, he obtained better resolved spectra by synchronously varying both the excitation and emission wavelengths.

The technique has since been used in various forensic science examinations such as drug analysis [2], comparison of oil spills with suspected sources [3], and possible identification of vehicles through the examination of oil drips, rubber from skid marks, and fluorescent tire prints [4-10]. Another source of forensic science comparisons is the rubber and rubber-like materials used in automobile bumper guards.

Recently, rubber and rubber-like materials have been increasingly used as bumper guards on automobiles of both foreign and domestic manufacture. Frequently these wrap around the front and rear to provide some side protection to the vehicle. Therefore, there is an increased chance of transfer or loss of this type of material in hit-and-run accidents.

Hueske and Clodfelter [11] used gas-liquid chromatography (GLC) to compare the thermal degradation products of rubber bumper guards from 19 different models of 1975 and 1976 American automobiles.

In the present study, SES was used to examine 56 bumper guard samples. The samples were primarily obtained from salvage yards near Frankfurt am Main, West Germany. The samples are listed in Table 1 and include bumper guard samples from automobiles

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TABLE 1—Automobile rubber bumper guards examined.^a

American Automobiles		
GM R-39 1970 Buick	AMC R-19 1975 Pacer	Chrysler R-33 1973 Chrysler
GM R-40 1972 Buick	AMC R-20 1975 Pacer	Chrysler R-34 1977 Plymouth
GM R-49 1973 Buick	AMC R-45 1974 Hornet	Chrysler R-41 1969 Dodge
GM R-50 1973 Buick	AMC R-47 1974 Gremlin	Chrysler R-58 1973 Plymouth
GM R-56 1974 Chev. Nova	AMC R-48 1973 Gremlin	Ford R-36 1974 Pinto
GM R-57 1973 Chev. Vega	AMC R-59 1975 Pacer	Ford R-51 1973 Mercury
	AMC R-60 1975 Pacer	Ford R-62 1973 Pinto
	AMC R-61 1974 Matador	Ford R-63 1973 Pinto
European Automobiles		
R-3 Audi, 1960	R-54 BMW, 1971	R-13 Renault 6
R-8 Audi, 1968 or 1969	R-24 Volvo	R-18 Renault 6
R-4 Mercedes, 1967 or 1968	R-28 Volvo	R-16 Citroen
R-6 Mercedes, 1964 or 1965	R-27 Saab	R-11 Peugeot 404
R-7 Mercedes, 1964 or 1965	R-65 Fiat, sports	R-17 Peugeot 404
R-14 Mercedes, 1967 or 1968	R-80 Skoda, 1978	R-29 Peugeot
R-26 Mercedes	R-73 Jaguar, 1978	R-42 Peugeot, 1972
R-30 Mercedes	R-10 Renault 16	R-55 Peugeot, 1974
R-23 VW, 411L	R-12 Renault 12	R-9 Simca 1000
R-25 VW, Beetle		
Japanese Automobiles		
R-22 Mazda	R-72 Toyota	R-35 Toyota Corolla, 1977
R-43 Mazda, 1975	R-67 Subaru	R-44 Toyota, 1972

^a Although more than 56 samples were collected, several samples appeared to be of plastic rather than rubber materials and were rejected.

of American, European, and Japanese manufacture. Since European automobile makers do not come out with new models each year, in many cases it was difficult to determine the year of manufacture.

Materials and Methods

Most samples required 1 mg or less of bumper guard material. The material was placed in a 12- by 75-mm disposable test tube and approximately 2 mL of dichloromethane (Merck, Art. 6050, zur Analyse, Lot 7465461) was added. (Although cyclohexane has been used by others as a solvent, this lot number of dichloromethane had a lower background fluorescence [Fig. 1]. Also, the dichloromethane was available in large supply since this laboratory was switched to using it where chloroform was used previously. Rubber samples soaked in dichloromethane produced fluorescence spectra similar, but not identical, to spectra of those samples soaked in cyclohexane.)

It was found that additional information could be obtained if the rubber samples were cut into very small pieces (0.1 mg or less) and then dropped into the test tube containing the dichloromethane. Based on their relative densities in dichloromethane, the 56 samples could be separated into three approximately equal categories. With 18 of the samples, the pieces floated and remained floating. With 19 other samples, the pieces floated initially but sank to the bottom as they became permeated with solvent (the tiniest and most thinly sliced pieces sank the fastest). With the remaining 19 samples, the pieces sank to the bottom in less than 5 s. Thus, in many cases, two samples could be distinguished by this preliminary treatment alone.

After a period of soaking (the time was not critical), the dichloromethane was transferred to a cuvette. After a scan by hand to find the maximum, the sample was diluted with

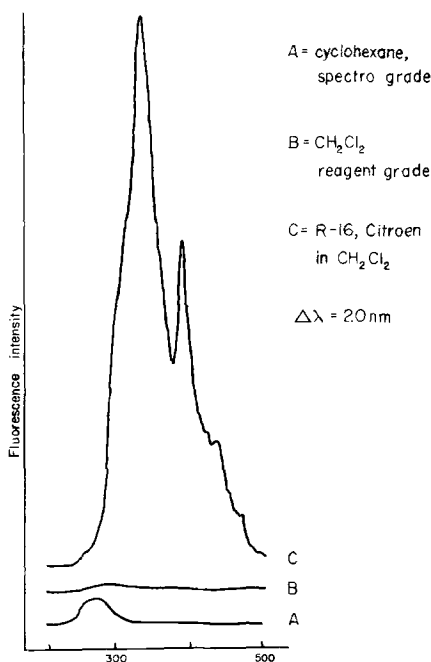


FIG. 1—Fluorescence emission spectra of spectrographic-grade cyclohexane (A), reagent-grade dichloromethane (B), and bumper guard sample R-16, Citroen, in dichloromethane (C), all synchronously excited at an interval of 20 nm.

dichloromethane until a maximum fluorescence intensity of 70 to 100% full scale was obtained at an instrument sensitivity setting of 10. (Samples should be compared at approximately equal and dilute concentrations since very concentrated solutions will produce distorted spectra.)

All fluorescence measurements were made with a Perkin-Elmer MPF-3 fluorescence spectrometer and were uncorrected for the spectral sensitivity distribution of the instrument. Instrument conditions were emission slit at 8 nm, excitation slit at 4 nm, chart speed at "low" (25 mm/min), and scan speed at 4. All samples were synchronously excited at an interval of 20 nm. This was accomplished by beginning each scan with the excitation at 200 nm and the emission at 220 nm. To operate synchronously, the "scan mode" switch must be in the "both" position. To begin a scan, the "wavelength drive" is switched from "off" to "excitation." Figure 2 shows some examples of the spectra obtained.

After the relative density in dichloromethane and the synchronously excited fluorescence emission spectra of all 56 samples had been obtained, those samples that were still not uniquely distinguishable from all others (see Table 2) were examined by using the GLC procedure of Hueske and Clodfelter [11].

The GLC analysis was performed on a Perkin-Elmer Model 900 gas chromatograph equipped with a flame ionization detector and a 1.8-m by 6.35-mm outside diameter glass column with 4% SE-30 on 80-100 mesh Chromosorb G, AW/DMCS. The column temperature was 80 to 250°C at 24°C/min, and injection port and manifold temperatures were 300°C. Dichloromethane was used as a solvent instead of carbon disulfide. The carrier gas was helium at a rate of 30 mL/min, and the chart speed was 10 mm/min.

Results and Discussion

At the outset of this study the following questions came to mind:

1. Could rubber from automobile bumper guards be differentiated by SES?
2. Could those rubber samples that gave similar patterns with SES be differentiated by GLC and vice versa?
3. Could SES identify the automobile manufacturer, or at least the rubber bumper guard manufacturer?

The experimental results indicate an affirmative answer to the first two questions but a negative answer to the third.

Of the 56 samples, all but 16 were uniquely distinguished by the combination of their relative densities in dichloromethane and SES. These remaining 16 arranged themselves into seven groups of two or three each (see Table 2). Although not available to the author, a double-beam instrument [12,13] or one capable of derivative techniques [14,15] could probably effect further discrimination.

All 16 of the remaining samples could be uniquely distinguished by the gas chromatographic procedure of Hueske and Clodfelter [11]. Thus, with the combination of

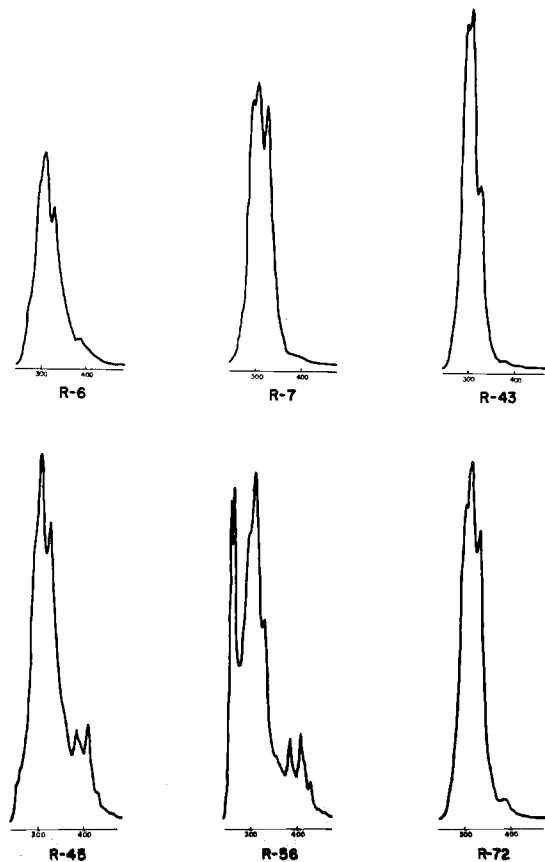


FIG. 2—Examples of synchronously excited (20-nm interval) fluorescence emission spectra of automobile rubber bumper guard samples (dichloromethane solvent).

TABLE 2—*Indistinguishable groups after combined relative density in dichloromethane and SES.*

Group	Group Members
1 ^a	R-6 (Mercedes), R-47 (Gremlin), R-44 (Toyota)
2 ^b	R-22 (Mazda), R-8 (Audi)
3 ^b	R-18 (Renault), R-13 (Renault)
4 ^b	R-17 (Peugeot), R-11 (Peugeot)
5 ^b	R-12 (Renault), R-10 (Renault), R-9 (Simca)
6 ^b	R-36 (Pinto), R-51 (Mercury)
7 ^c	R-34 (Plymouth), R-65 (Fiat)

^a All pieces floated in dichloromethane.

^b All pieces sank in dichloromethane.

^c Pieces first floated and then sank in dichloromethane.

their relative densities in dichloromethane, SES, and GLC, all 56 samples were uniquely distinguishable. The three tests seem to be completely independent.

A few rubber samples were examined by GLC both before and after they had been soaked in dichloromethane. The GLC patterns produced were similar but not identical. Thus, if one had a very limited sample, all three tests could be performed on the same material if the comparison standard were to be treated in the same manner.

Hueske and Clodfelter [11] found that their 19 samples could be grouped into General Motors, Ford, Chrysler, or American Motors products with the exception of rubber removed from two 1976 Dodge Colts that could not be distinguished from the General Motors automobiles. No such pattern emerged from the examination of the 56 samples by SES. Samples from automobiles made in different parts of the world might have similar SES patterns (for example, the Mazda, R-22, and the Audi, R-8), while rubber samples taken from different pieces on the same automobile might give quite different SES patterns (as shown in Fig. 2, R-6 was from the front bumper and R-7 from the rear bumper of the same Mercedes).

Most of the SES patterns that were obtained from different automobiles of the same manufacturer were distinguishable. According to Lloyd [4-10], most of the fluorescence from tire rubber is due to extender oils, antidegradants, and polynuclear hydrocarbons. Thus, minor variations in the proportion of these materials or changes in the source of supply may produce different SES patterns even though the basic formulation remains the same.

The author has written to 24 automobile manufacturers in an attempt to learn what companies supply them with rubber bumper guards. From the 14 responses received to date, it appears that many automotive manufacturers have several different suppliers. Also, it would appear that only rarely do different automotive manufacturers receive their rubber bumper guards from the same supplier. One response indicated that between 3000 and 5000 pieces might be made in one production run.

Thus, although the SES pattern obtained is a class rather than individual characteristic, it is a characteristic of that particular production run for that piece, rather than for a particular make, model, and year of automobile.

Summary

Fifty-six automobile rubber bumper guard samples were examined by SES using a dichloromethane solvent. Additional information was obtained during sample preparation by noting their relative densities in dichloromethane.

All 56 samples could be uniquely distinguished by the combination of their relative

densities in dichloromethane, SES, and GLC of their thermal degradation products.

Although SES is capable of differentiating between automobile rubber bumper guard samples, it does not appear capable of identifying the automobile or bumper guard manufacturer. Thus, in hit-and-run accident cases, SES would be of little value in providing investigative leads, but it could be of value once the investigation has focused on a particular suspect vehicle.

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References

- [1] Lloyd, J. B. F., "Synchronized Excitation of Fluorescence Emission Spectra," *Nature Physical Science*, Vol. 231, May 1971, pp. 64-65.
- [2] Andre, J. C., Baudot, P., and Niclause, M., "Application of Synchronous Excitation Spectrofluorimetry to Drug Analysis," *Clinica Chimica Acta*, Vol. 76, No. 11, Nov. 1977, pp. 55-66.
- [3] John, P. and Soutar, I., "Identification of Crude Oils by Synchronous Excitation Spectrofluorimetry," *Analytical Chemistry*, Vol. 48, No. 3, March 1976, pp. 520-524.
- [4] Lloyd, J. B. F., "The Nature and Evidential Value of the Luminescence of Automobile Engine Oils and Related Material, Part I. Synchronous Excitation of Fluorescence Emission," *Journal of the Forensic Science Society*, Vol. 11, No. 2, April 1971, pp. 83-94.
- [5] Lloyd, J. B. F., "The Nature and Evidential Value of the Luminescence of Automobile Engine Oils and Related Material, Part II. Aggregate Luminescence," *Journal of the Forensic Science Society*, Vol. 11, No. 3, July 1971, pp. 153-170.
- [6] Lloyd, J. B. F., "The Nature and Evidential Value of the Luminescence of Automobile Engine Oils and Related Material, Part III. Separated Luminescence," *Journal of the Forensic Science Society*, Vol. 11, No. 4, Oct. 1971, pp. 235-253.
- [7] Loughran, J. H., Lloyd, J. B. F., and Watson, T. R., "Murder Involving Discovery and First Application of Fluorescence of Tyre Prints," *Nature (London)*, Vol. 250, No. 5469, Aug. 1974, pp. 762-764.
- [8] Lloyd, J. B. F., "Characterization of Rubbers, Rubber Contact Traces and Tyre Prints by Fluorescence Spectroscopy," *Analyst*, Vol. 100, No. 1187, Feb. 1975, pp. 82-95.
- [9] Lloyd, J. B. F., "Luminescence of Tire Marks and Other Rubber Contact Traces," *Journal of the Forensic Science Society*, Vol. 16, No. 1, Jan. 1976, pp. 5-19.
- [10] Lloyd, J. B. F., "Make the Traces Glow," *Industrial Research*, Vol. 19, No. 12, Nov. 1977, pp. 29-32.
- [11] Hueske, E. E. and Clodfelter, R. W., "An Examination of Selected Automobile Rubber Bumper Guards," *Journal of Forensic Sciences*, Vol. 22, No. 3, July 1977, pp. 636-638.
- [12] Madlin, H., Cravitt, S., Kallet, E., and Dachs, M., "A New Dual-Beam (Differential) Spectrofluorometer," presented at the 1976 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, 1-5 March 1976.
- [13] Sheridan, J. and Jadamec, J. R., "Oil Fingerprinting Using Double-Beam Fluorescence," presented at the 1976 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, 1-5 March 1976.
- [14] Green, G. L. and O'Haver, T. C., "Derivative Luminescence Spectrometry," *Analytical Chemistry*, Vol. 46, No. 14, Dec. 1974, pp. 2191-2196.
- [15] Terhaar, D. A. and DiCesare, J. L., "Derivative Techniques Used with Fluorescence Applications," presented at the 1979 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, 5-9 March 1979.

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