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E. L. Covey,[1] *B.S.*

Application of Energy Dispersive X-Ray Spectroscopy in Fire Investigation

The classic examination of arson-related evidence in the forensic science laboratory strives to identify the particular accelerant employed by the perpetrator. Very often this is not possible because of the complete combustion of that accelerant, loss of the unburned accelerant because of evaporation, or loss in the mechanics of extinguishing the fire.

It has been observed in the Metropolitan Kansas City, Missouri region that in approximately 90% of the arson cases submitted, gasoline was the suspected or implied accelerant. In 100% of the arsons where gasoline was identified, it was determined to be a leaded gasoline. Energy dispersive X-ray spectroscopy (EDX) can be employed to detect the residual combustion products of the antiknock formulations of leaded gasolines as they occur on the various types of building materials and debris encountered in the laboratory [*1,2*].

Technical and Experimental Procedure

Alkyl leads and bromides are commonly added to raw gasolines to obtain proper octane ratings. These additives may be incorporated in raw gasolines to concentrations of 1 to 3 g as free lead and 17% ethylene dibromide per gallon of the marketed product.[2]

Open air combustion of these gasolines results in a nonvolatile residue which includes readily detectable concentrations of lead bromides. A controlled study was conducted by applying 2 ml of a leaded gasoline to approximately 1 in.^{2} (6 cm^2) of various building materials and substrates and allowing them to burn until the flames exhausted themselves. After air drying the sample until no hydrocarbons could be detected by gas chromatographic analysis, the burned remains were then subjected to EDX analysis for lead and bromine. Each sample was complemented with a common-origin standard which was analyzed before any burning and again after burning in the absence of gasoline.

The instrument was a Finnigan Model No. 77-80 EDX spectrometer and data system with a rhodium target and filter. Each sample was counted for 300 s with operating conditions of 40 kV and the milliamperage adjusted to a dead time of 40%.

The controlled study also included restricting the application area of the leaded gasoline on the material to observe any diffusion of this residue as the burning progressed. Table 1 lists the materials employed in the controlled study and the results of both the restricted and unrestricted area tests.

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[1] Chief forensic chemist, Regional Criminalistics Laboratory, Metropolitan Kansas City, Mo. 64051.

[2] J. Lampkin, Amoco Oil Company Refinery, Sugar Creek, Mo., personal communications, March 1976.

TABLE 1—*Results of the restricted and unrestricted area tests in the controlled study.*

		Unrestricted Area Study			Restricted Area Study	
Material	Analysis	Unburned Standard	Burned Standard Without Leaded Gasoline	Combustion with Leaded Gasoline	Area of Accelerant Combustion	Area of Combustion Without Accelerant
Wood (painted)	lead	+ + +	+ + +	+ + +	+ + +	+ + +
	bromine	−	−	+ +	+ +	−
Wood (unpainted)	lead	−	−	+ +	+ +	−
	bromine	−	−	+ +	+ +	−
Carpet	lead	+	+	+ + +	+ + +	+
	bromine	+ +	+ + +	+ + +	+ + +	+ +
Clothing (various fibers)	lead	−	−	+ + +	+ + +	−
	bromine	−	−	+ + +	+ + +	−
Plastic	lead	−	−	+ +	+ +	−
	bromine	−	−	+ +	+ +	−
Tile	lead	+	+	+ + +	+ + +	+
	bromine	−	−	+ +	+ +	−
Foam rubber	lead	−	−	+ + +	+ + +	−
	bromine	−	−	+ + +	+ + +	−
Naugahyde®	lead	−	−	+ +	+ +	−
	bromine	−	−	+ +	+ +	−
Brick (various)	lead	+	N/A	+ +	+ +	+
	bromine	−	N/A	+	+	−
Stone	lead	+	N/A	+ +	+ +	+
	bromine	−	N/A	+	+	−
Metallic surfaces	lead	+	N/A	+	+	+
	bromine	−	N/A	+	+	−
Rope (hemp)	lead	−	−	+ + +	+ + +	−
	bromine	−	−	+ + +	+ + +	−
Insulation material	lead	−	N/A	+ + +	+ + +	−
	bromine	−	N/A	+ + +	+ + +	−
Glass	lead	+	N/A	+	+	+
	bromine	−	N/A	+	+	−
Papers (various)	lead	−	−	+ +	+ +	−
	bromine	−	−	+ +	+ +	−

− = negative
\+ = trace
\+ + = moderate
\+ + + = heavy
N/A = not applicable

Case Report

Analysis by EDX for lead and bromine has been performed on 385 arson cases involving 878 examinations. One such case involved the burning of an apartment by a tenant. Through investigative efforts by police department personnel, the suspect was alleged to have angrily thrown gasoline about the livingroom carpeting and set it ablaze. Examination of the livingroom carpeting did reveal several individual spot-like burns varying in size from approximately 1 in. to 4 ft (25 mm to 1 m) in diameter. Samples from these burned areas and standards of unburned carpeting were collected. Gas chromatographic examination of the samples for volatile components of an accelerant was unsuccessful. This probably was caused by the three to four-day time lapse between the fire and sample collection.

Analysis by EDX of a section of the burned areas of carpeting readily detected lead and bromine, as shown in the spectra in Fig. 1. A 1-in. (25-mm) square section of the unburned carpet standard was burned in the absence of gasoline and subjected to EDX analysis identical to the questioned sample above. No lead or bromine could be detected in the standard even with an extension of counting time (Fig. 2). A comparison of the evidentiary sample over the standard sample is shown in Fig. 3.

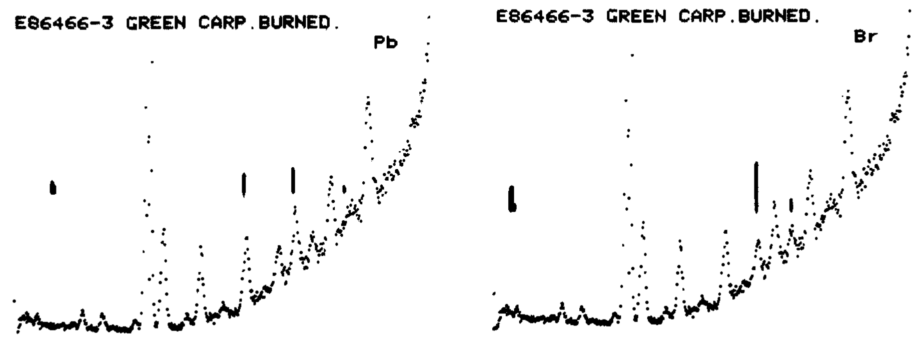

FIG. 1—*Cathode-ray tube displays of questioned carpet sample. Operating conditions: 40 kV, 0.10 mA with a 100-s count.*

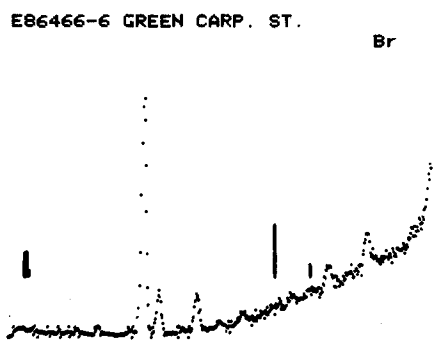

FIG. 2—*Cathode-ray tube display of carpet standard burned in the absence of gasoline. Operating conditions: 40 kV, 0.3 mA with a 300-s count.*

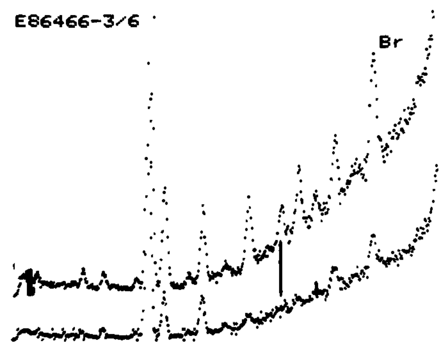

FIG. 3—*Cathode-ray tube display of spectrum of the questioned sample over spectrum of the standard.*

Discussion

Evaluation of EDX as a supplemental approach to the problem of evaluation of evidence submitted in fire investigations has included a controlled study as well as application to evidence from 385 individual cases of suspected arson over a 28-month period. The method has served particularly well as a supplement to volatile residue analysis in demonstrating that the hydrocarbon-aromatic fractions detected are from a gasoline and not from some other product containing similar petroleum distillates.

The method has also proven to be applicable as an additional tool after attempts to detect volatile residues have failed. The presence of lead bromide in the absence of the volatile residues is indicative of the burning of a leaded gasoline. The alkyl leads and bromines are converted to the involatile lead bromide through the combustion process. The mere application of a leaded gasoline to a sample area does yield detectable quantities of the two elements; however, both the lead alkyls and the ethylene dibromide are volatile and therefore will evaporate with time and be lost in the same manner in which the hydrocarbon-aromatic fractions evaporate.

The use of common-origin standards in conjunction with questioned samples cannot be overemphasized. While throughout this study no standards contained lead and bromine which would be mistaken for the additive residue, some materials can contain one or both of the two elements of interest. Some samples having leaded paints associated with them would yield extremely high concentrations of lead but would still allow the detection of bromine in the instance of an unknown. Several carpeting samples would yield high concentrations of bromine and, being usually contaminated with soil, would quite often have low concentrations of lead. To date, the interpretation of the presence of lead and bromine from this type of sample has posed no problem. The standards have served in determining whether or not the levels and ratios of lead and bromine are consistent with the additive residue.

The substrate material on which the gasoline is being burned has a large effect on the amount of lead bromide retained. The higher-surface-area, absorbent materials such as clothing and carpeting retain as much as three times the lead bromide as does a flat-surfaced, nonabsorbent material such as glass or metal. It is thought that this phenomenon is attributable to the vapors being trapped within the "pockets" of the material matrix and being burned there as opposed to escaping from volatilization. In addition, the possibility of selective sorption in the skin layers of fibers of synthetic and natural polymeric materials because of the difference in morphology and physical structure is well known. This sorption may account for the preferred presence and retention of lead and bromine.

The lead-bromine levels occurring with flat-surfaced, nonabsorbent materials are sufficient for detection with EDX with limits of approximately 0.70 $\mu g/cm^2$ for lead and bromine. These limits do vary, depending on the matrix of the sample. This approach is not applicable to nonleaded gasolines because the octane ratings required are achieved through blending of high octane number hydrocarbons rather than additives.

Summary

The detection of lead bromide on the burned remains in suspected arson cases can be interpreted as being indicative of the burning of a leaded gasoline when the proper controls and standards are provided. The presence of the lead bromide also supplements the detection of hydrocarbon-aromatics in the sample, thus confirming the volatiles as having originated from a leaded gasoline. This method can also provide a means of screening where large quantities of evidence are encountered.

Acknowledgments

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References

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Regional Criminalistics Laboratory
2100 N. Noland Rd.
Independence, Mo. 64051