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Characterization of Paint Fragments by Combined Topographical and Chemical Electron Optics Techniques

Automotive paint fragments are one type of physical evidence material which has been examined by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDS) [*1,2*]. The SEM-EDS can add to the information which can be obtained from a paint sample because the paint contains both topographical features and chemical composition data. Previous research has been undertaken to try to understand the nature of the variables involved and the criteria of data evaluation [*1–4*]. While these studies showed the applicability of the SEM to the forensic science analysis of paint fragments, the questions of reproducibility of the data obtained and of reliability as an identifying technique were not definitively answered.

The experimental approach was to examine paints of the same color because in actual application, paints of different color could already be optically distinguished before SEM-EDS analysis was attempted. Additionally, because spectra in previous studies of the same color paints, particularly the work done with white paint, had shown general similarities [*1*], a comparison of spectra taken from different portions of the same sample with spectra from other similarly colored paint sources could serve as a test for both the reproducibility of spectra and for the reliability of making positive comparisons of two spectra from the same source.

Experimental Procedure

Paint chip samples from four vehicles having a similar blue exterior were selected and mounted for examination in the SEM. The samples were coded in terms of their sources as follows: Source 31, 1970 Ford Maverick; Source 32, 1968 Plymouth Roadrunner; Source 33, 1969 Chevelle; and Source 34, 1970 Plymouth Valiant. This study was primarily concerned with different aspects of reproducibility and reliability of X-ray spectra data obtained; therefore, only a limited number of samples was employed. Previous investigations performed under this research program have examined topography and composition of paint samples from more than 100 vehicles.

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Three chips of paint from each source were used: one mounted with its exterior surface up, one with the interior or primer surface up, and the third mounted on edge. The specimens were evaporator coated with carbon to provide conductivity without introducing additional X-ray peaks.

There were three stages of data acquisition. The first was topographical examination of the three chips from each source. Secondary electron micrographs at ×700 were taken to record the observed topographies. A Materials Analysis Corporation Model 700 Scanning Electron Microscope, equipped with a Kevex-Nuclear Data Energy Dispersive X-ray Spectrometer System, was employed.

The second stage of data acquisition was the accumulation of spectra from the exterior and primer surface. A computer interfaced, energy dispersive, X-ray detection system was employed for this purpose. A 0–10 keV spectrum was recorded for each surface, either for a specified time at a given count rate, or until there were a specified number of counts in the maximum channel of a particular peak. The spectra could thus be collected in a way which facilitates both visual and numerical comparisons. In addition, up to three separately collected spectra, from the same or from different samples, could be simultaneously displayed either superimposed or displaced slightly with respect to one another. These modes of display employed the ability of data storage and variable displacing capabilities of a computer oriented, data acquisition system. Other manipulations could be performed, including expanding portions of spectra to facilitate peak recognition and subtracting one spectrum from another to emphasize differences between spectra. These first two stages were conducted twice for each specimen during separate data acquisition sessions.

The third stage of the process was carried out on those samples in which the chemical composition spectra showed similarities both in the elements present and the values of the peak heights of the major elements in the spectrum. All of the exterior surfaces from each of the sources studied contained the same four major elements—aluminum, silicon, sulfur, and chlorine. In order to facilitate comparisons and to bring out any minor peaks which might be present, long-time counts were taken so that spectra were accumulated until there were 8000 counts in the peak channel of the aluminum peak. Two of these extended time spectra were taken and recorded for each sample. Because the primer side spectrum varied sufficiently between sample sources, this step was not required for spectra from the primer sides.

Results

The samples in this study yielded data, both topographical and spectral, which were reproducible and characteristic of the source from which the data were obtained. In all cases, the two sets of micrographs from the same source showed strong resemblance, especially when contrasted with the topographical data of other sample sources from this and previous studies. While the similarity is based on subjective evaluation, there were many topographical features which could be used in the comparisons.

The chemical composition spectral data were also reproducible. Figure 1 shows spectra taken from two different locations in the same general area of an exterior surface, which have been expanded and displaced with respect to one another to show the reproducibility of peak heights. Before displacement the two spectra superimposed so completely that it was impossible to determine that there were two spectra in the display. Figures 2 and 3 show two spectra acquired at different times from different locations in the same area of a primer surface.

The comparison of spectra from the primer side of different sources revealed that the spectra could characterize the source. The primer side spectra were clearly different for

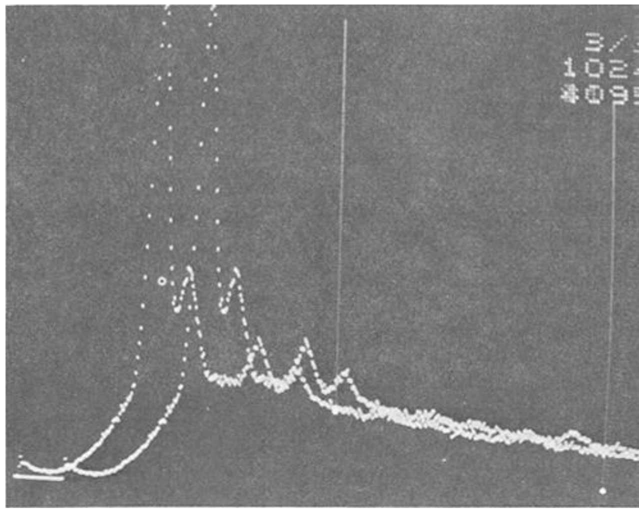

FIG. 1—*Two expanded (0–5 keV) and displaced exterior spectra from the same source (Number 31). Peaks (left to right) are Al, Si, S, and Cl.*

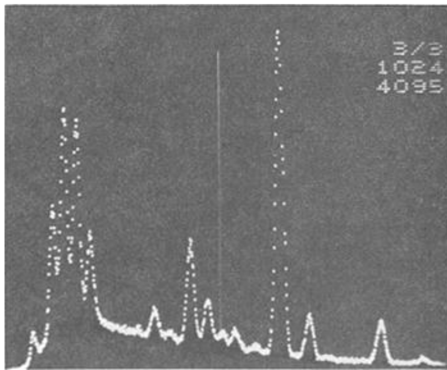

FIG. 2—*Primer side spectrum of Source 33. Peaks (left to right) are Zn Lα, Al, Si, P, S, Cr, Ba L series, Cr, Fe and Zn.*

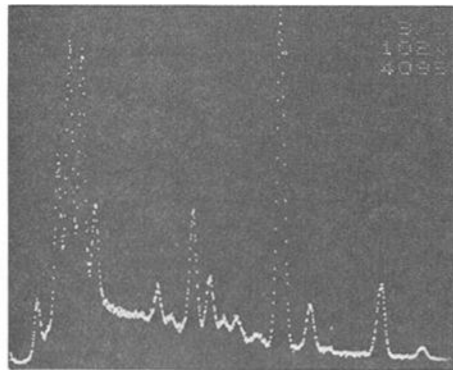

FIG. 3—*Second primer side spectrum of Source 33 showing the same peaks present as in Fig. 2.*

each sample source. The spectrum in Fig. 4 is distinct from the ones in Figs. 2 and 3. Comparison of the chemical compositions of these two primer samples based upon these spectra alone could differentiate between the two sources. Differences in the chemical content of the primers are readily apparent by this procedure. The exterior surface spectra, however, all contained the same four major elements and generally contained no obvious distinguishing features (Figs. 5 and 6). The type of data obtained from the long-time spectra becomes valuable for this case. This is because in the long-time data acquisition, any differences in the minor elements become more apparent relative to the background level of the spectrum. This is due to the improvement in the statistical quality of the data with additional counting time. In the shorter time data acquisition, unless the composition differences are marked, the differences in the spectrum are not immediately evident. Figure 7 is a simultaneous, slightly displaced display of two exterior spectra from different sources.

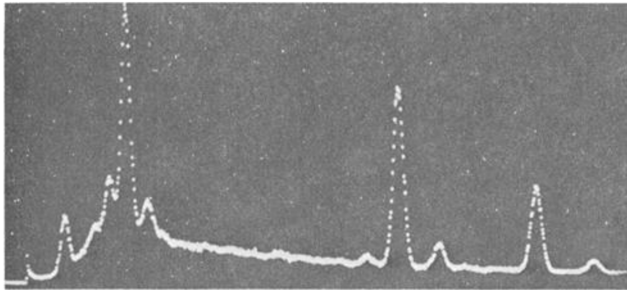

FIG. 4—*Primer side spectrum of Source 31. Peaks (left to right) are Zn Lα, Al, Si, P, S, Mn, Fe Kα and Kβ, and Zn Kα.*

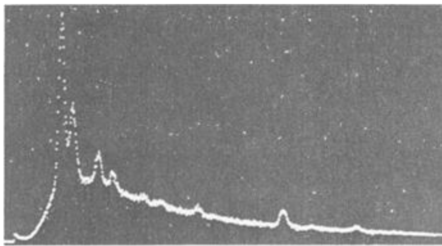

FIG. 5—*Exterior spectrum of Source 31. Prominent peaks (left to right) are Al, Si, S, Cl, Ba, Fe, and Cu.*

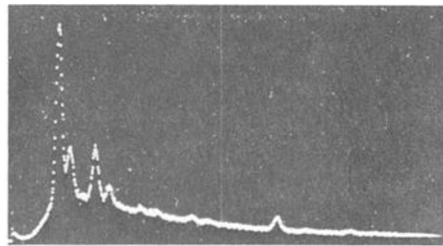

FIG. 6—*Exterior surface spectrum of Sample 34. Prominent peaks (left to right) are Al, S, Cl, Si, Ba, Fe, and Cu.*

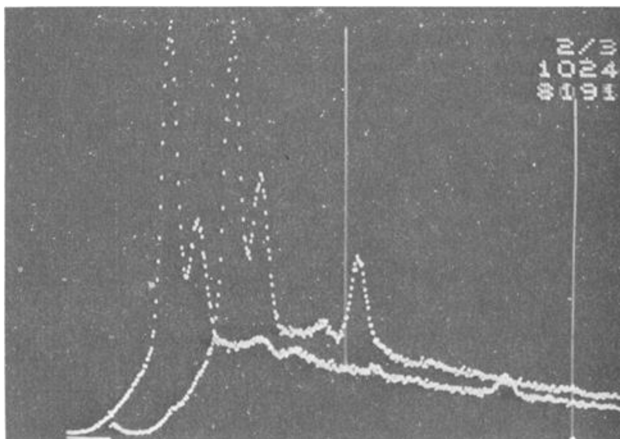

FIG. 7—*Expanded and displaced spectra of Sources 32 (right) and 33 (left).*

In Fig. 8, one spectrum has been subtracted from the other to show where, in terms of the X-ray spectra, the compositions varied significantly.

Table 1 summarizes the numerical data recorded from the extended time spectra. The major elements are those in which peaks were many times background, while the minor elements showed a lower peak-to-background ratio. Except for one peak of a minor element, which apparently was not high enough above background to be recorded, the data

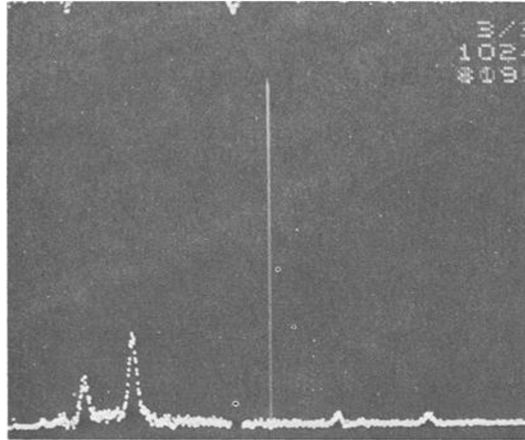

FIG. 8—*Channel by channel difference of the spectra in Fig. 7. The peaks remaining are due to variations in Si, Cl, and Ba (inverted peak at top) concentrations.*

were excellent on a semi-quantitative basis for the first three sources. All count values were within approximately 10 percent in comparing the two spectra of each sample, while varying by substantially greater amounts between samples from the different sources. In the fourth source, the difference in counts is large but uniformly higher for all peaks, except aluminum in the 34-2 as compared to the 34-1 data. If one multiplies the low count totals by 1.85, the variance is in the range of that for other sources. It should be noted, however, that despite the variations in this sample a careful comparison of spectra would lead to correct pairing of the two samples from the same source.

Discussion

The topographical features observed in the four specimens were characteristic of the sources and by themselves were sufficient to distinguish the individual sources from one another. There are, however, as previous work has shown [*1,2*], many cases in which topography is insufficient for matching of samples from the same source. Figures 9 and 10 show two similar exterior surfaces from different sources and Figs. 11 and 12 show two

TABLE 1—*Data recorded from the extended time spectra.*

Sample Number	Major Elements (counts in peak channel)				Minor Elements[a]				
	Al	Si	S	Cl	K	Ba	Fe	Cu	Zn
31-1	7998	3591	2442	1946	X	X	X	X	–
31-2	7999	3482	2231	1855	–	X	X	X	–
32-1	8001	5541	2454	3654	X	–	X	X	–
32-2	7999	5062	2112	3506	X	–	X	X	–
33-1	8006	3959	1829	1647	X	X	X	X	–
33-2	8002	4198	1938	1672	X	X	X	X	–
34-1	8002	2728	2521	1525	X	X	X	X	X
34-2	8000	5228	4509	2771	X	X	X	X	X

[a] X = peak for this element detected above background.
– = peak not detected.

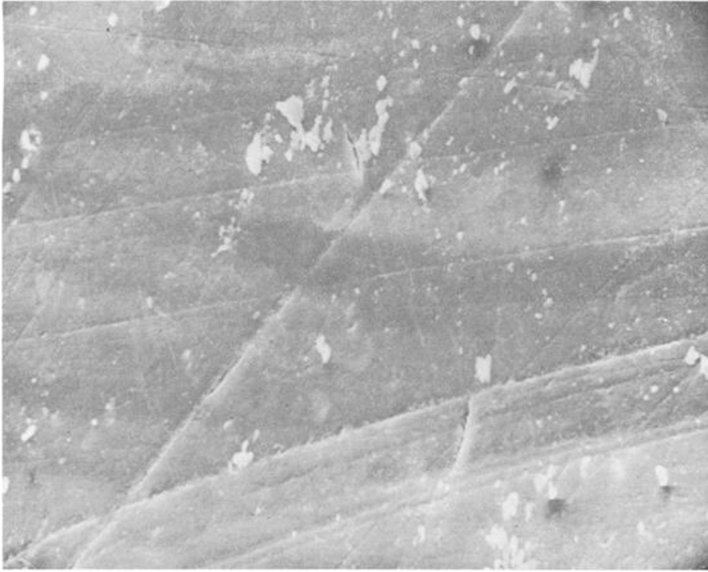

FIG. 9—*Source 32 exterior surface (original magnification ×700).*

FIG. 10—*Source 34 exterior surface (original magnification ×700).*

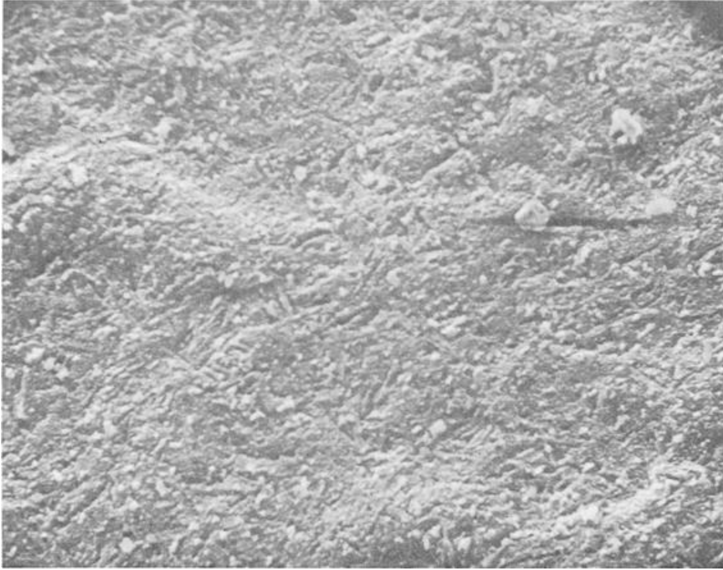

FIG. 11—*Source 33 primer surface (original magnification* $\times 700$*).*

FIG. 12—*Source 34 primer surface (original magnification* $\times 700$*).*

similar primer surfaces from different sources. Without further data (either edge micrographs or spectra) these topographies would be inadequate to distinguish between the sources because they both have the same general class characteristics.

The spectra provide an additional source of information which can aid in this procedure. The characteristic X-ray spectrum generated from a paint chip is due to the interaction of electrons with the elements in the microvolume bombarded. The individual X-ray peak heights are a function of the chemical composition in that microvolume. Thus, the X-ray data obtained from a paint chip place it in a class with other paint surfaces containing the same major elements in the same approximate peak height ratios, since it is an intrinsic physical characteristic of the matter present. When there is also a detectable minor element spectrum, either due to the presence of additive or of contaminants, then the population to which the source could possibly belong is reduced. Further, the spectra from other paint layers present, such as the primer, may yet greatly narrow the size of the class to which this sample can belong. In the limit, these source population reductions may result in the individualization of the paint chip as coming from a given source.

The spectra were reproducible, with one exception in which a primer side spectrum showed a very large iron peak in one spectrum and a significantly smaller iron peak in the second. This could be explained by the fact that in removing the paint chip at the paint-metal interface, varying amounts of underlying metal may have been lifted with the chip. Careful examination of the spectra show that all other elements are in similar ratios to each other in the two cases, with only the iron peak varying greatly. In addition to indicating the importance of sample collection and preparation, this example implies the sensitivity of this method and the significance of spectra that are highly similar as being characteristic of the sample source. Additionally, this observation suggests that to avoid difficulties due to composition variations on the microscale, a method be employed wherein spectra are taken at several different points on each paint chip. Subsequently, these spectra could be averaged, eliminating by an inspection of data obtained a spectrum judged to be nonrepresentative.

When the SEM-EDS method of matching a sample to a sample source is employed, a combined evaluation of all available topographies and spectral data, in addition to other available analytical techniques, is necessary. The comparison of topographies and spectra depends on the experience and judgment of the investigator, the degree to which certain features characterize a sample, and the sample preparation and data collection procedures.

Conclusions

A limited study of paint samples has yielded topographical and spectral data which are reproducible and characteristic of the sample source. While there are generally obvious distinctions between data from different sources, the matching of samples to a sample source with SEM-EDS techniques is a difficult process requiring examination of all available data, and requiring experience and judgment on the part of the investigator. The use of spectral acquisition and analysis techniques which examine several points on each sample surface, allows for a compositional characterization of the paint chips for use in subsequent comparison procedures.

Summary

The application of scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDS) to automotive paint samples has yielded information of significant potential value in forensic science investigations. In order to evaluate data, however, the

inherent variation of composition and topography must be better understood. This is especially true in the case of X-ray spectra, which contain intrinsic statistical fluctuations.

Paint samples were examined in this study with the specific aim of characterizing the reliability and reproducibility of the X-ray spectra obtained. Samples of the same color paints were chosen to test the SEM-EDS system with paint samples that are very similar and, consequently, difficult to distinguish by current color comparison techniques. Data, in the form of secondary electron micrographs and X-ray spectra, were acquired and comparisons among samples were made. Minor elements present in the external paint layer and the variations in primer layer were of principal interest in composition analysis.

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