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The Application of a Multistylus Recorder to the Energy Dispersive Analysis of Paint Flakes in the Scanning Electron Microscope

Paint flakes occur as evidence in a wide variety of crimes. Here we shall confine ourselves to the examination of vehicle paints, although the methods are equally applicable to other types of paint.

Analysis of a fragment of paint left at the scene of a vehicle accident can sometimes provide a clue to the offending vehicle's color, make, and model. Once a suspect vehicle has been located samples of its paint are compared with the paint found at the scene. If a comparison of the flakes with an optical microscope shows half-a-dozen or more matching layers there is a very high probability that the flakes had a common origin. However, if fewer layers are present further characterization of layers is desirable. Commonly, infrared spectroscopy or pyrolysis gas chromatography is used to give information on the type of resin; these methods are destructive and difficult to apply to small specks or smears and require physical separation of the layers in multilayered flakes. Analysis of the inorganic constituents, for example by emission spectroscopy, provides extra discrimination but is generally a bulk property and of little use for multilayered flakes of various thicknesses.

Several aspects of the examination of paint flakes with the scanning electron microscope (SEM) have been reported [*1-9*], and the electron microprobe has also been used for paint layer analysis [*10,11*]. The primary electron beam of the SEM causes secondary electrons to be emitted from the surface under study and these are collected to form an image of the surface; in addition, characteristic X-rays are excited from elements close to the surface. An energy dispersive X-ray analyzer enables all elements within a broad spectral energy range to be detected simultaneously.

Here we report the use of a multistylus chart recorder to display any variations in the spectrum as the electron beam is scanned along a line on the specimen, thus providing a compositional profile. This provides a rapid, nondestructive, semiquantitative analysis of the inorganic constituents of paint layers even in damaged flakes, minute specks, or smears which are not amenable to most other techniques. Studies were made of the ability of the method to discriminate between flakes.

Experimental Procedure

Paint flakes were mounted on double-sided Sellotape® on graphite blocks and coated with a thin conducting layer of carbon by vacuum deposition.

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Samples of a flake were mounted to show a freshly cut edge and the topcoat and primer surfaces. Surface topographies and analyses were generally observed with a magnification of ×700.

Samples of well-stirred liquid paint collected from the assembly plants were spotted on graphite blocks and baked to manufacturers' specifications. They were found to give the same analyses as samples of the same paints from factory-sprayed plates.

The Japan Electron Optics Laboratories (JEOL) JSM-U3 scanning electron microscope, fitted with an EDAX® energy dispersive X-ray (EDX) analyzer, was operated with an accelerating voltage of 25 kV and a beam current on the order of 10^{-9} A to give a count rate on the order of 1000 counts per second.

The Auckland Nuclear Accessory Company (ANAC) Model 910 multistylus chart recorder has 128 writing channels (each 2 mm in width) across the electrosensitive paper. The spectrum of pulse heights seen at the detector output is digitized, and each pulse is routed to a channel whose position on the paper is proportional to X-ray energy. Each X-ray photon triggers a writing pulse which produces an immediately visible dot in the appropriate channel.

The chart drive is synchronized with the electron beam, which is slowly scanned along a chosen line on the specimen, producing a compositional profile in which the energy and intensity of the X-rays generated are recorded as a function of the position on the specimen. In the records obtained the vertical axis represents distance along the scan line of the specimen, and the horizontal axis represents X-ray energy. Each of the 128 writing channels acts as a recording ratemeter for a narrow band of X-ray energies, the dot density or blackening at any point on the record thus being related to the X-ray intensity emitted at the corresponding point on the specimen. The operation and some applications of this recorder have been described elsewhere [*12-14*].

Results and Discussion

Reproducibility and Discrimination

A preliminary investigation of the potential reproducibility and discrimination of the method was made on paint flakes collected in a wrecker's yard.

Four samples were taken from different parts of the same white car. The chart records of these specimens are shown in Fig. 1. In spite of the variation in thickness and the nonhomogeneity of the layers there is little difficulty in visually assessing the pattern and drawing the conclusion that the four samples could have come from the same car.

Repeat analyses along the same line of the specimen were reproducible, provided that the accelerating voltage and beam current were unchanged. Closely spaced scans gave similar results when the recorder was used to enable the effect of nonhomogeneity to be compensated.

To test discrimination between different cars, flakes were taken from 15 light blue cars of similar color. These were analyzed with the multistylus recorder, and the records of a number of them are shown in Fig. 2. All of the 15 flakes were distinguishable on the basis of these analyses, with specimens that had primer layers being easily and rapidly distinguished.

The chart records show that the major inorganic component in the topcoat was titanium, with barely detectable traces of aluminum, sulfur, silicon, chlorine, calcium, iron, and zinc. In some cases certain trace elements were found in small clusters rather than distributed homogeneously through the layer, with elements such as calcium and sulfur being found with each other. Inhomogeneities in the primer layers were more marked, perhaps because of particles of larger sizes and varying densities.

Clearly, during normal EDX spot or area analyses inclusions could lead to nonrepre-

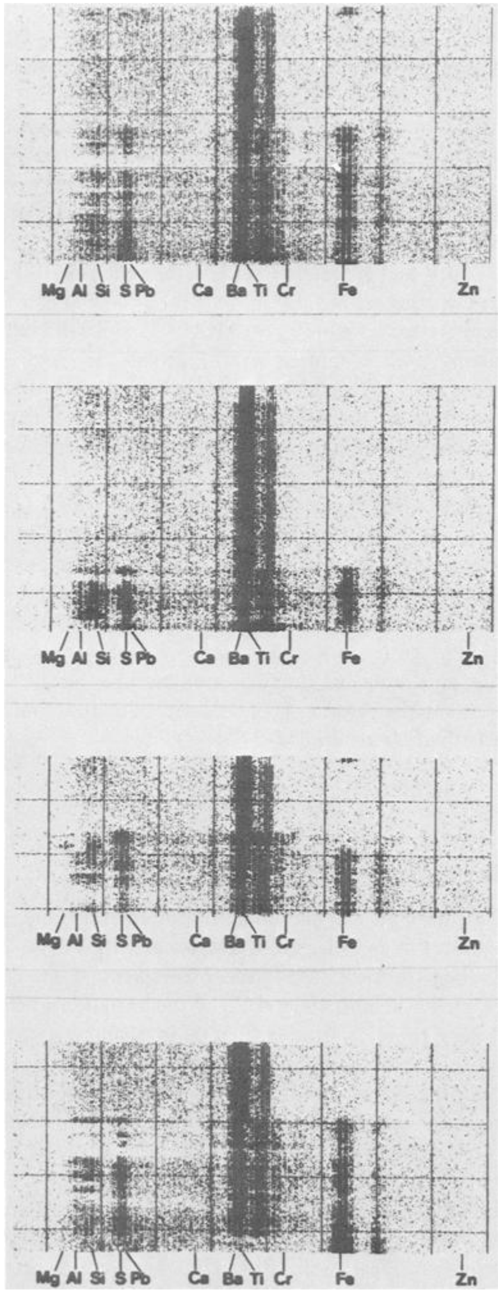

FIG. 1—*Spectra of flakes from different parts of the same car.*

sentative spectra and hence several different areas would need to be examined. The multistylus recorder is able to give a reproducible, representative spectrum and locate and analyze impurities. In fact, the degree and type of inhomogeneity observed on the charts can even be an additional distinguishing characteristic of the sample; for example, pigments settling to the bottom of a layer may show the number of coats of the same paint that had been applied.

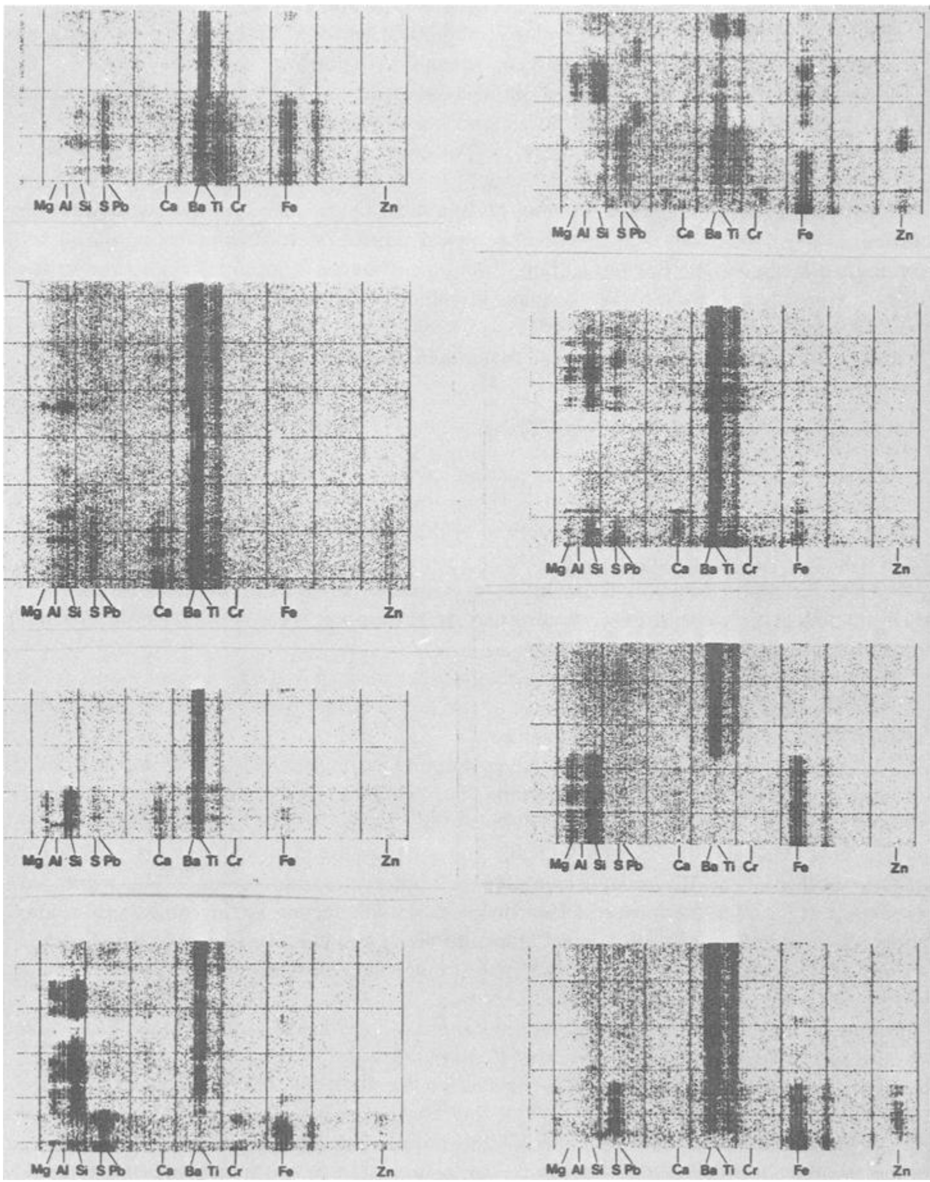

FIG. 2—*Spectra of whole flakes from wrecker's yard cars.*

Comparison with Other Methods

An attempt was made to distinguish between the blue topcoats, on the basis of the type and concentration of trace elements, by accumulating a large number of counts with the EDX analyzer. Four of the 15 topcoats had slight differences in the trace element pattern, which enabled them to be distinguished. In the remaining paints the peak-to-background ratios were so low that the differences were not significant. The semiquantitative nature of the spectra shown on the multistylus chart recorder appears to be adequate and little is gained from using the more quantitative conventional display.

Examination of the topcoat surface at a magnification of ×700 enabled a further three samples to be distinguished on the basis of unusual topography.

A combination of visually observed surface discoloration, topography, and analysis left 4 indistinguishable topcoats out of the 15 topcoats of originally indistinguishable color.

Primers are generally either red or gray, and therefore little discrimination can be made on the basis of color. Analysis of the resin[3] enables the primers to be considerably subdivided, but in cases of smears or small multilayered flakes such an analysis may be very difficult. All of the primers in the wrecker's yard samples were readily distinguished with the multistylus recorder. Barium sulfate, calcium carbonate, titanium dioxide, and various silicate minerals appeared to be the main inorganic constituents. Zinc chromate was present in some primers and iron oxide in the red ones. Conventional EDX analysis of primers suffers from the limitations of reproducibility previously described.

Discrimination of Current Production Paints

Almost the entire automotive paint market in New Zealand is supplied by two manufacturers having a total of 15 different primers. Analysis of samples of these showed that they were composed of various combinations of the same basic components as the wrecker's yard samples. All but three of the wrecker's yard samples could be identified with current primers; the unidentified ones could be nonautomotive primers or earlier versions of current primers. Twelve of the 15 current primer samples were distinguishable by their multistylus chart records.

To investigate the potential of the method for discriminating between topcoats we collected and analyzed some 60 samples of the liquid paints used in 1975 by the five car-assembly plants in the Auckland province.

The spectra were divided into four main groups according to the major elements present. Group A comprises those paints containing lead, while in Group B the paints contain iron but no lead. The paints in Group C contain titanium but no iron or lead. Group D comprises those topcoats that contain no lead, iron, or titanium. The groups were further subdivided according to the amount and type of other elements present. The results are presented in Fig. 3 in the form of a flow diagram suitable for use in the computerized identification of vehicle make and model from the elemental composition of a paint sample. Group D is omitted from Fig. 3 for clarity, but it contained two metallic paints distinguishable by a trace amount of lead in one.

Table 1 shows the relationship between the EDX groups and the color of the paint (according to the *Methuen Handbook of Colour*) [*15*].

Many of the paints were similar in color and could be difficult to distinguish in a crime exhibit such as a paint smear. The EDX analysis was most useful for distinguishing between green paints (probably because of the number of different pigment combinations which produce a green color). Shades of red, yellow, and brown paints were fairly readily distinguished by EDX. There is not a direct correlation between EDX analysis and color, and the two properties can complement each other. A given EDX spectrum could be consistent with several different colors, but if an optical match is first obtained then the EDX analysis can provide extra discrimination (see range of analytical groups for each hue in Table 1). However, blues, pastels, and whites are generally indistinguishable by EDX and analysis will be of little evidential value unless an unusual pigment is found (which may imply an older type of paint or an architectural paint).

[3] R. H. Meinhold, unpublished results.

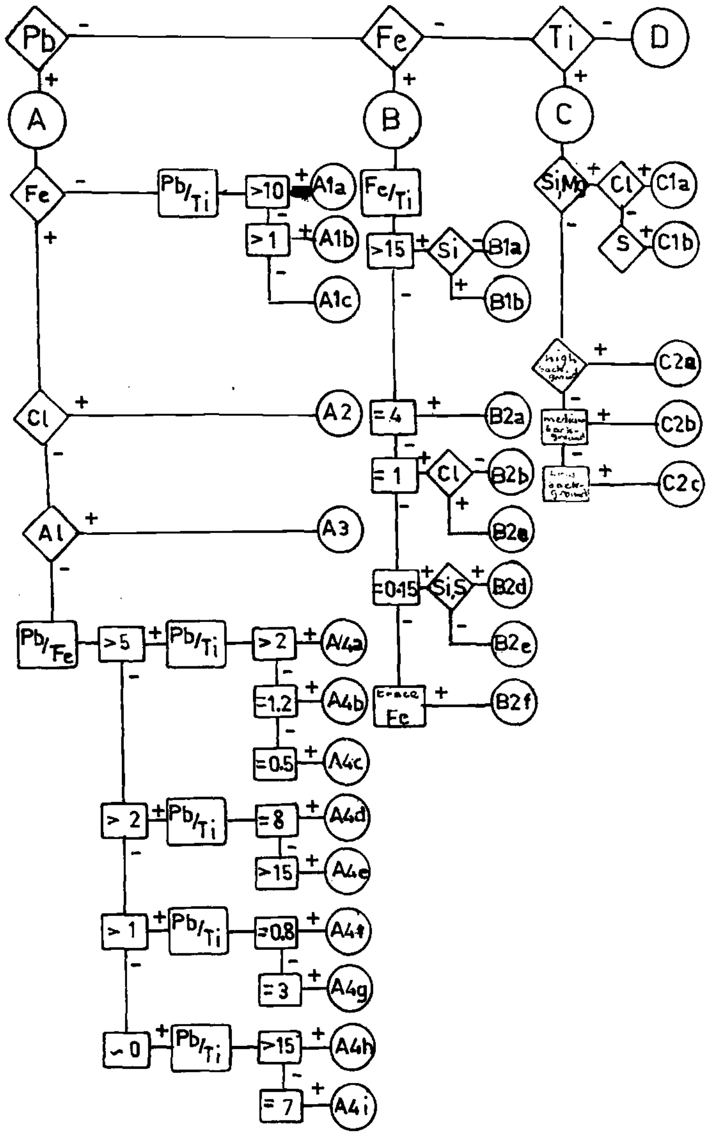

FIG. 3—*Flow diagram relating the analysis to the analytical group of the topcoats.*

We found that lacquers and baking enamels of the same color generally gave the same spectra, but in one instance the same orange-brown color produced in both lacquer and enamel by one manufacturer and in lacquer by another gave slightly different analyses for each paint.

While many aspects of surface structure or layer texture can be examined optically the SEM can often show greater and clearer details such as the type of diatoms present in some fillers. Elemental analyses in the SEM may often be useful in identifying an interesting surface feature, as in the case of a network of crystalline material, embedded in a paint layer, which was shown to be zinc phosphate arising from the initial metal treatment by a particular factory.

TABLE 1—*Relationship between EDX analysis and color of topcoats.*

Color	Hue [*15*]	Analytical Group
Blue	20	1, C2a
Blue	21	2, C2b
Blue	22	1, C2b
Blue	23	1, C2b; 1, C2c; 1, D1
Turquoise	24	1, C2b; 1, D2
Bluish green	25	1, C1a
Green	26	1, C2b
Green	27	1, B2d
Green	28	1, A3
Yellowish green	29	0
Yellowish green	30	1, A4c; 1, A4d; 1, B1a; 1, B2b; 1, C2c
Greenish yellow	1	2, C2c
Yellow	2	1, A1c; 1, C1b
Yellow	3	1, A4a; 1, B2e; 1, B2f; 1, C2c
Orange yellow	4	1, A4f; 1, B2c; 2, B2e
Orange	5	1, A4a; 1, A4i; 1, B2a
Orange	6	1, A1a; 1, A1b; 1, A4d; 1, A4e; 1, A4h
Reddish orange	7	1, A1a; 1, A4b
Reddish orange	8	1, A1a; 1, A4g
Red	9	0
Red	10	2, A1a; 2, A1b; 1, B1b; 1, B2a
Red	11	1, A1b; 1, A2
Red-blue	12–19	1, D1
White		1, C2b; 5, C2c

Conclusions

Energy dispersive X-ray analysis with the SEM is a rapid and nondestructive method of identifying the main elements in the organic pigments, fillers, and impurities in paint samples. The method does not appear to be sufficiently sensitive to identify minor pigments or to detect the expected batch-to-batch variations in trace elements or pigment ratios; we are investigating the applicability to New Zealand paints of the more sensitive technique of X-ray fluorescence spectroscopy (for example, see Ref *16*), though the types of specimen that can be handled are limited.

Elemental analysis in the SEM is of the most value in the analysis of samples such as small specks or smears where conventional analyses are not possible and in the analysis of flakes with only a few layers where extra discrimination can be obtained by a nondestructive analysis prior to conventional infrared, pyrolysis gas chromatography, or other destructive analyses.

Although primers are generally only red or gray they show a wide range of constituents. Analysis of the primer layer enables many primers to be distinguished and may enable a particular paint manufacturer's product, and hence the type of vehicle on which it was used, to be identified.

The EDX spectra of the topcoats are not independent of color, but they can enable some shades, particularly reds or greens, to be discriminated; shades of blues or whites are difficult to distinguish.

Multistylus records of paint flakes with primer layers provide high discrimination between samples.

The multistylus recorder enables the elemental composition of paint layers to be compared semiquantitatively but avoids the problems inherent in EDX analyses resulting from the nonhomogeneous nature of the sample. The recorder is most useful for the analysis of multiphase or nonhomogeneous samples, the main advantages being these:

(1) the detection of small particles rich in particular elements (those inhomogeneities can further characterize a sample and may be missed altogether or cause unreproducible spectra in a conventional analysis), and

(2) simple, rapid, and reproducible acquisition of permanent semiquantitative compositional profiles of multiphase specimens.

Summary

A scanning electron microscope with energy dispersive X-ray analysis provides a rapid and nondestructive means of identifying the main elements in each layer of even the most minute paint flakes. A novel multistylus chart recorder enables all elements in a specimen to be continuously analyzed semiquantitatively as a function of position on the specimen. This reduces the problems usually associated with the analysis of nonhomogeneous samples such as paint layers and enables potentially characteristic surface contaminants and matrix inclusions to be easily located for further analysis and visual study.

A survey of some paints from both new and older cars has shown that most paints can be differentiated with this technique.

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