TECHNICAL NOTE

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The Application of Mass Spectrometry to the Study of Pencil Marks

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ABSTRACT: Organic mass spectrometry offers a possible method for distinguishing between pencils by examination of the material transferred to paper in a single written letter. In a preliminary selected ion recording experiment, marks made by 17 different pencils were divided into four groups. Problems were encountered, however, when attempts were made to apply the technique to pencil writing on hard or soiled paper.

KEY WORDS: questioned documents, spectroscopic analysis, pencils

A recent study of pencils carried out from the point of view of forensic scientists by Cain et al [*1*] has prompted us to report some preliminary experiments which show that discrimination between pencils can be achieved by an examination of pencil marks. Cain et al [*1*] suggested various techniques that might in the future be used to examine either the inorganic components or the wax components of pencil marks but pointed out the problems that arise as a consequence of very small quantities of material available. Organic mass spectrometry is a highly sensitive technique not mentioned by Cain et al [*1*] that we have applied to the problem with some success.

The mass spectra of pencil cores as we have recorded them are essentially mixed spectra of the waxes used in the manufacturing process. Cain et al [*1*] have discussed the waxes used and have achieved some discrimination between pencils by thin-layer chromatography (TLC) of the waxes. However, the TLC technique is not sufficiently sensitive for the examination of pencil marks. The differences in mass spectra that might be exploited are illustrated in Figs. 1 to 3, which show typical full spectra of powdered samples (approximately 100 μg) from the cores of three different pencils. The sensitivity of mass spectrometry may be greatly enhanced by the use of the selected ion recording (SIR) technique, and discrimination between marks on paper then becomes possible on the basis of the relative intensities of various ions.

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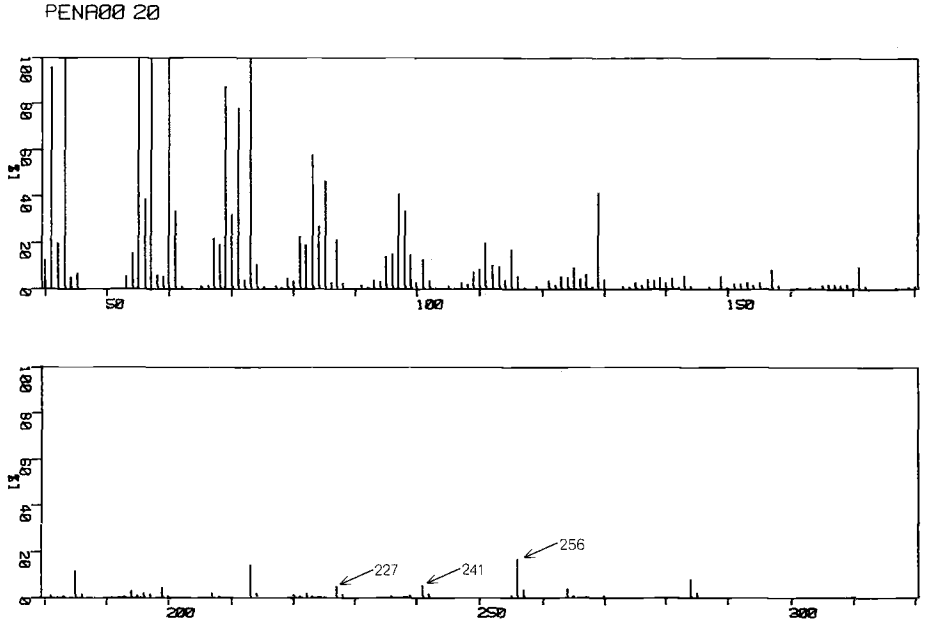

FIG. 1—*Full mass spectrum of a Group A pencil core.*

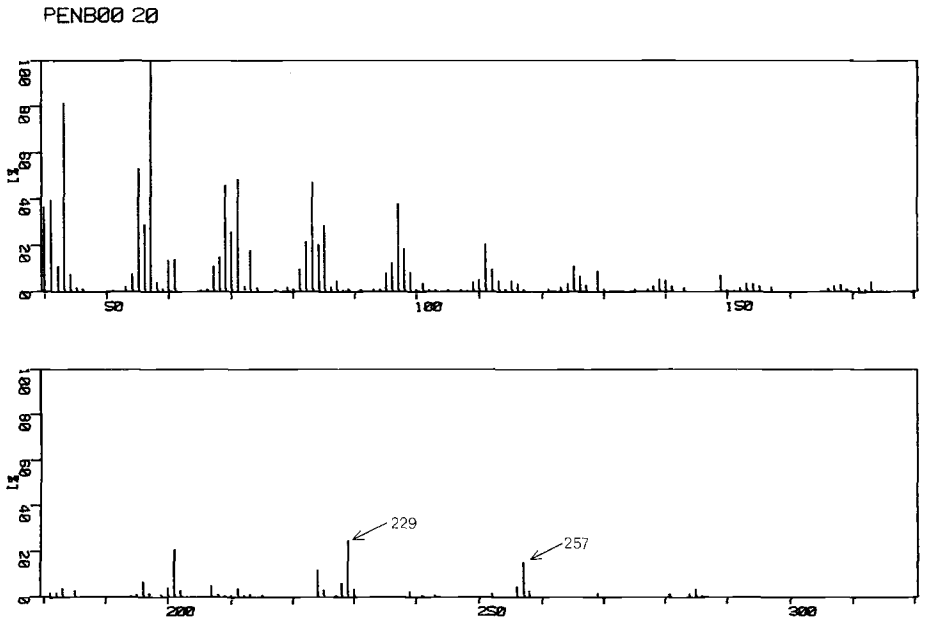

FIG. 2—*Full mass spectrum of a Group B pencil core.*

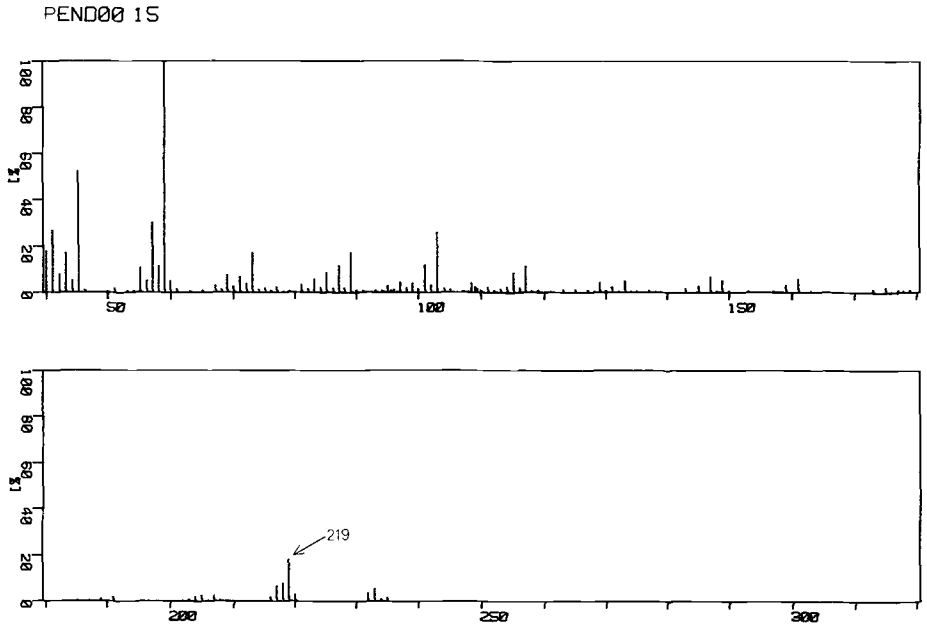

FIG. 3—*Full mass spectrum of a Group D pencil core.*

Method

The mass spectrometer (VG Micromass 12F) was operated in the SIR mode to monitor the ions at *m/e* 219, 227, 229, 239, 241, 256, 257, and 264 generated by electron impact ionization. Ions in this region are not the most intense in the spectra, but they offer the possibility of discrimination and suffer less from background interference from paper than lower mass ions. The stability of the instrument in switching between these ions was easily checked by the introduction of the common reference compound heptacosafluorotributylamine, which gives intense ions at *m/e* 219 and 264. The samples were introduced to the spectrometer by means of a direct insertion probe fitted with a glass sample tube of internal diameter about 1.2 mm. Heat to volatilize the samples was provided by the source block, which was maintained at 260°C.

Pencil marks were removed from paper by scraping the surface with a blade to produce a ball of fibers that was then lodged inside the sample tube near the open end. After insertion of the probe the eight ions were monitored for about 5 min, during which time the intensities of particular ions rose to a peak (sometimes two peaks) and fell again. For each sample an unmarked area of paper surface immediately adjacent to the pencil mark was scraped off and examined in the same way to eliminate the contribution of traces of volatile organics in the paper.

Results and Discussion

A small collection of 17 pencils of various brand names and hardness designations was examined. Marks in the form of the capital letter *A* (about 7 by 3 mm) were made with a firm writing pressure on a soft high rag content paper containing little or no organic or inorganic filler. The results obtained from these marks suggested that the technique was sufficiently sensitive to permit the use of considerably smaller or fainter marks. The marks (and

TABLE 1—*Discrimination among pencils by SIR of marks on paper.*

Group	Pencils in Group	Most Significant Ions, *m/e*
A	7	227, 241, 256
B	5	229, 257
C	4	...
D	1	219

therefore the pencils) could be clearly divided into four groups. Table 1 shows these groups and their most distinctive ions. One pencil from each of Groups A, B, and D was used to produce the spectra shown in Figs. 1, 2, and 3, respectively. The spectra of the Group C pencils were essentially the same as the Group A pencils but about an order of magnitude weaker for an equivalent amount of pencil core. There was no apparent correlation between hardness designation and the group classification.

The pencil marks remained easily distinguishable by SIR mass spectrometry for several months but no attempt has as yet been made to verify the homogeneity of pencils along their length.

These results suggest that the application of organic mass spectrometry to the problems of distinguishing between marks made by different pencils could yield a useful method. However, in attempting to apply the method to the types of marks of interest to forensic document examiners, several problems have become apparent. When the paper on which a mark was made was soiled or had been much handled the mass spectrometric features of the mark were obscured by skin oils or other materials on the fibers scraped up with the mark. The degree of separation of a pencil mark from the underlying paper achieved by scraping with a blade was not good, but when the paper was soft a satisfactory ball of fibers could be produced and transferred to the sample tube. With hard papers this proved impossible, and scraping often yielded only a fine gray dust that was difficult to handle.

While this method has potential, some improvement is clearly necessary before it can be routinely applied to normal case material. A better technique for the separation of the marks from paper and for transferring the separated mark to a sample tube would be of great value. Work will continue on this and other improvements, including the investigation of ions other than those monitored in the present study and of the application of other mass spectrometric techniques such as computer averaging of full spectra.

Reference

[*1*] Cain, S., Cantu, A. A., Brunnelle, R., and Lyter, A., "A Scientific Study of Pencil Lead Components," *Journal of Forensic Sciences,* Vol. 23, No. 4, Oct. 1978, pp. 643-661.

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