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Analysis of Ballpoint Pen Inks by Field Desorption Mass Spectrometry

REFERENCE: Sakayanagi M, Komuro J, Konda Y, Watanabe K, Harigaya Y. Analysis of ballpoint pen inks by field desorption mass spectrometry. J Forensic Sci 1999;44(6):1204–1214.

ABSTRACT: Destructive identification of ballpoint pen ink was performed using field desorption mass spectrometry (FDMS) to determine the basic dyes in ballpoint pen ink. Seven different brands of black, blue, and red ballpoint pen inks (total: 21 samples) were examined in this study. A 1-mm section was cut from an ink line drawn on paper and used as the sample. Extraction was performed with methanol. Analysis of each extract by FDMS showed the molecular ion peak of each dye and the black, blue, and red inks were then classified into 6, 6, and 6 types, respectively, based on the ions detected. The results indicated that it was possible to distinguish between manufacturers of ballpoint pens. This analysis of ballpoint pen inks was found to be effective and the method was applied to the analysis of an actual forensic sample.

KEYWORDS: forensic science, questioned documents, ballpoint pen ink, mass spectrometry, Field Desorption

Analysis of ballpoint pen ink on questioned documents is often required in the field of forensic science in order to identify the writing implement used in the commission of a crime. Usually such examinations of ballpoint pen ink are entrusted to the laboratory in the form of a written sample on paper. In forensic work, it is thus necessary to identify the manufacturer of the pen or the specific ink product.

The initial analysis of ballpoint pen ink is carried out using nondestructive methods such as visible, ultraviolet, and infrared light examination. However, nondestructive methods are useful only for answering the question of whether two or more documents could have the same origin. When more detailed information is required, some form of destructive chemical examination must be used.

The solvent used in ballpoint pen ink volatilizes gradually. However, the non-volatile nature of the dyes in these inks makes the dyes very valuable to the forensic scientist because the dyes remain on paper in the form of letters, marks or lines after the solvent has evaporated. Thin layer chromatography (TLC) (1–5) is widely used in forensic science because it does not require special apparatus and has the advantage of providing simple and direct operation. However, the information provided by TLC is limited to the color tone and Rf value, so this method is not suitable for identifying ballpoint pen inks. Analysis by high-performance liquid chromatography (HPLC) (6–7) has also been reported. Furthermore, Fourier transform infrared absorption spectrometry (FTIR) (8) has been also used for the identification of ballpoint pen ink.

The inks used in ballpoint pens contain basic dyes among others and these dyes are non-volatile. Some of the basic dyes used in ballpoint pen ink are shown in Fig. 1. These dyes have a characteristic structure containing an iminium group and benzene and naphthalene rings together with an extended conjugated system. The non-volatile character of the basic dyes is due to their cationic part.

Mass spectrometry by electron impact and chemical ionization has not been widely applied for the analysis and identification of ballpoint pen ink because of the volatility requirement. In contrast, field desorption mass spectrometry (FDMS) is a useful ionization method that is well suited to the analysis of non-volatilizeable compounds such as basic dyes. In this report, FDMS was used to identify the basic dyes in ballpoint pen inks. FDMS of several basic dyes has already been reported (9), however, ours is the first report concerning the systematic analysis of the basic dyes in ballpoint pen ink and its application to forensic samples.

Materials and Methods

Materials

Eight standard color dyes used for ballpoint pen ink were examined and their structures and names in the Color Index are shown in Fig. 1. These dyes were kindly supplied by the manufacturers (Hodogaya Chemical Co., Ltd. Yokohama, Japan; Taoka Chemical Co., Ltd. Osaka, Japan; BASF Japan Ltd. Tokyo, Japan) or by the Criminal Investigation Bureau, National Police Agency, Tokyo, Japan. Twenty-one ballpoint pens were used for this study. Samples consisted of commercially available black, blue, and red ballpoint pens from each of seven Japanese pen manufacturers. Analytical grade methanol (Wako Pure Chemical Industries, Ltd., Osaka, Japan) was used for extraction.

Extraction Technique

Samples were obtained as follows. A straight line was drawn on white copy paper with each of the 21 ballpoint pens described above. An ink line 1 mm in length was cut from the drawn line and placed in a glass capillary tube with an inside diameter of 1 mm and with one end closed. Extraction was performed with methanol (2 μL) at room temperature for 10 min. The methanol solution containing the extracted dyes was then applied on the emitter for analysis.

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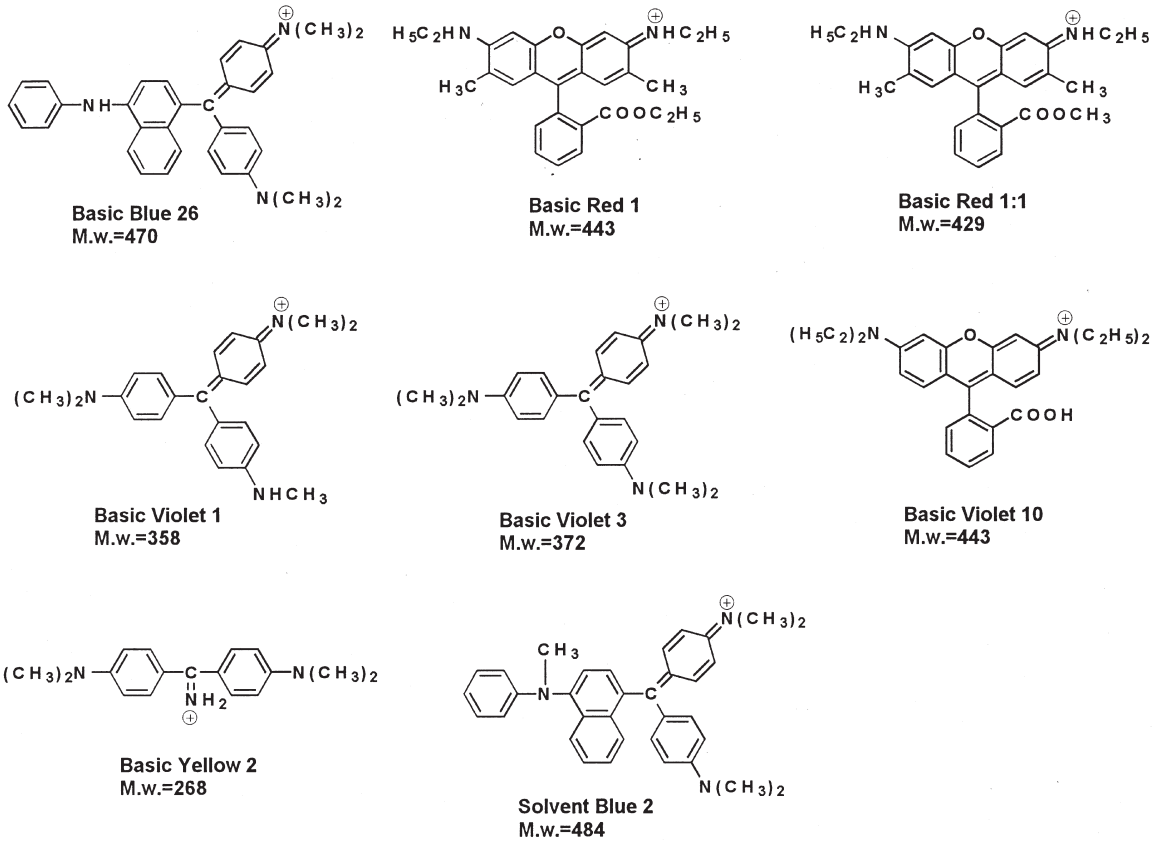

FIG. 1—*Structures of dyes used in ballpoint pen inks.*

Conditions for Mass Spectrometric Analysis

Mass spectra were obtained with a JMS-AX505HA magnetic sector mass spectrometer (JEOL Ltd., Tokyo, Japan). The instrument was operated at an acceleration potential of 3 kV with a cathode voltage of −5 kV. A source heater was not used and the source temperature was 25°C. Tuning of the probe and instrument were achieved by using the m/z 58 ion of acetone generated by field ionization. Carbon was used for the emitter. The emitter current was swept from 0 to 40 mA at 2 mA/min. Mass calibration was performed with an Ultramark 1621 by fast atom bombardment ionization.

Results and Discussion

Mass Spectrometric Analysis of Color Dyes

The field desorption (FD) mass spectra of eight color dyes are shown in Figs. 2 to 9. As can be seen from the mass spectra, molecular ions were observed as the base peaks from each dyes, except for Basic Violet 1 (Fig. 6). The above results demonstrated that the FD Mass spectra of the basic dyes examined in this study show a molecular ion as the base peak. Thus, FDMS is suitable for examining mixtures of dyes without the need for preprocessing such as chromatographic separation.

Basic Violet 1 was an exception containing other molecules. Basic Violet 1 is ordinary offered as a mixture of N-hexa-methyl, penta-methyl, and tetra-methyl derivatives (10) whose molecular ions correspond to m/z 372, 358, and 344, respectively. Therefore the FD mass spectrum of Basic Violet 1 gave m/z 372 (base peak), 358 and 344 ions (Fig. 6). The reason why the molecular ions of Basic Violet 3 was detected as a base peak is that Basic Violet 3(M^+, m/z 372) seems to be predominant to Basic Violet 1(M^+, m/z 358).

Furthermore, quantitative ratio of Basic Violet 1 and Basic Violet 3 was measured by ^{1}H-NMR spectrum and the ratio was approximately 1 to 1.4. In fact, the ion of m/z 372 is detected as the base peak is quite reasonably.

Mass Spectrometric Analysis of Ballpoint Pen Inks

Black Ballpoint Pen Inks—The analysis was performed for the purpose of classifying the black ballpoint pen inks from the seven manufacturers based on the results of FDMS. The FD mass spectrum of a typical black ballpoint pen ink is shown in Fig. 10. The m/z 443 and m/z 429 ions correspond to the molecular ions of Basic Red 1 and Basic Red 1:1, respectively. It was clarified that same ballpoint pen inks contain blue and red basic dyes. The black inks from the seven manufacturers were analyzed and the ions detected are summarized in Table 1. The black ballpoint pen inks were classified into six types (Type I~VI). It should be noted that the Black-F ink did not contain basic dyes (see Table 1).

Blue Ballpoint Pen Inks—The FD mass spectrum of a typical blue ballpoint pen ink is shown in Fig. 11. These m/z 344, 358, and 372 ions all originated from Basic Violet 1, and the m/z 470 ion corresponds to Basic Blue 26. The blue ballpoint pen inks from the seven manufacturers were analyzed and the ions detected are summarized in Table 2. The Blue ballpoint pen inks were classified into six types (Type I~VI).

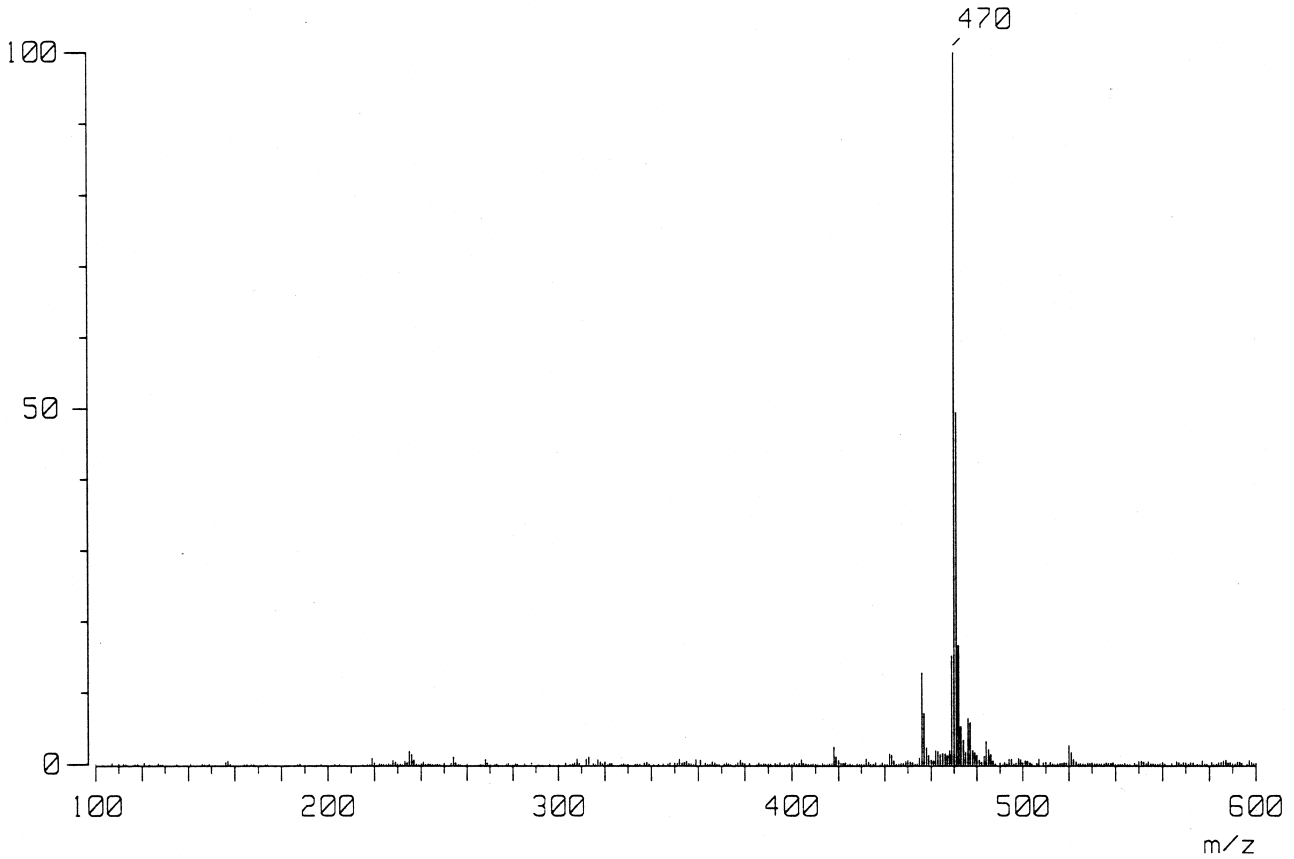

FIG. 2—*FD mass spectrum of Basic Blue 26.*

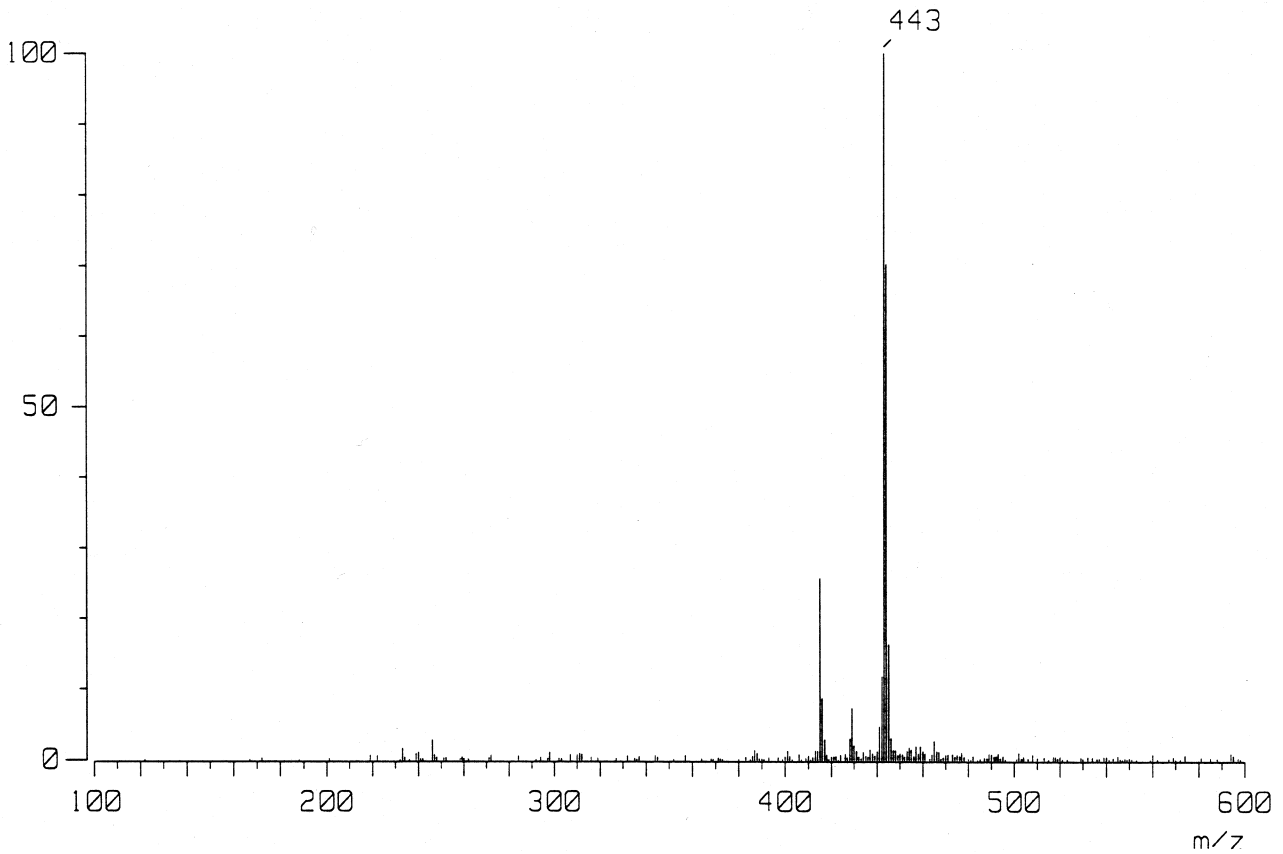

FIG. 3—*FD mass spectrum of Basic Red 1.*

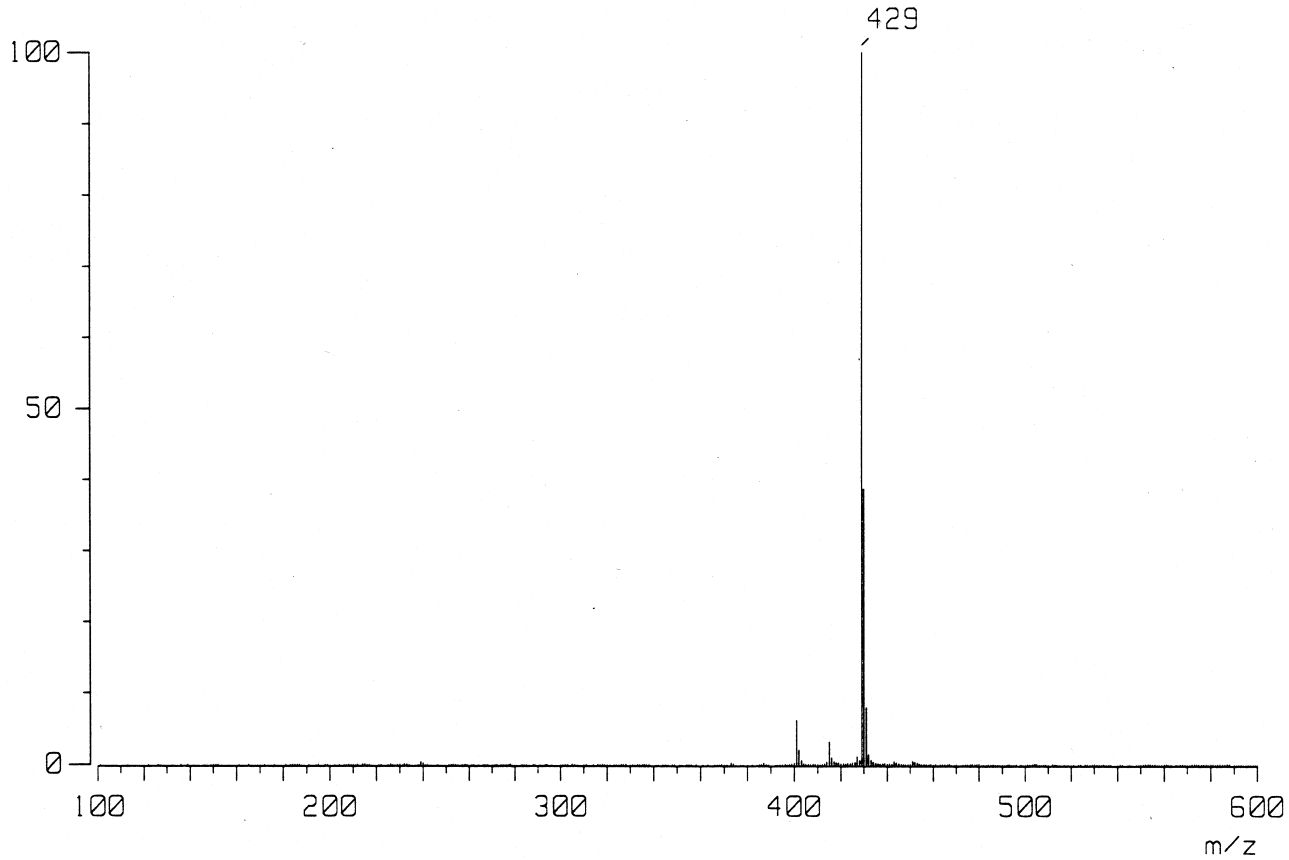

FIG. 4—*FD mass spectrum of Basic Red 1:1.*

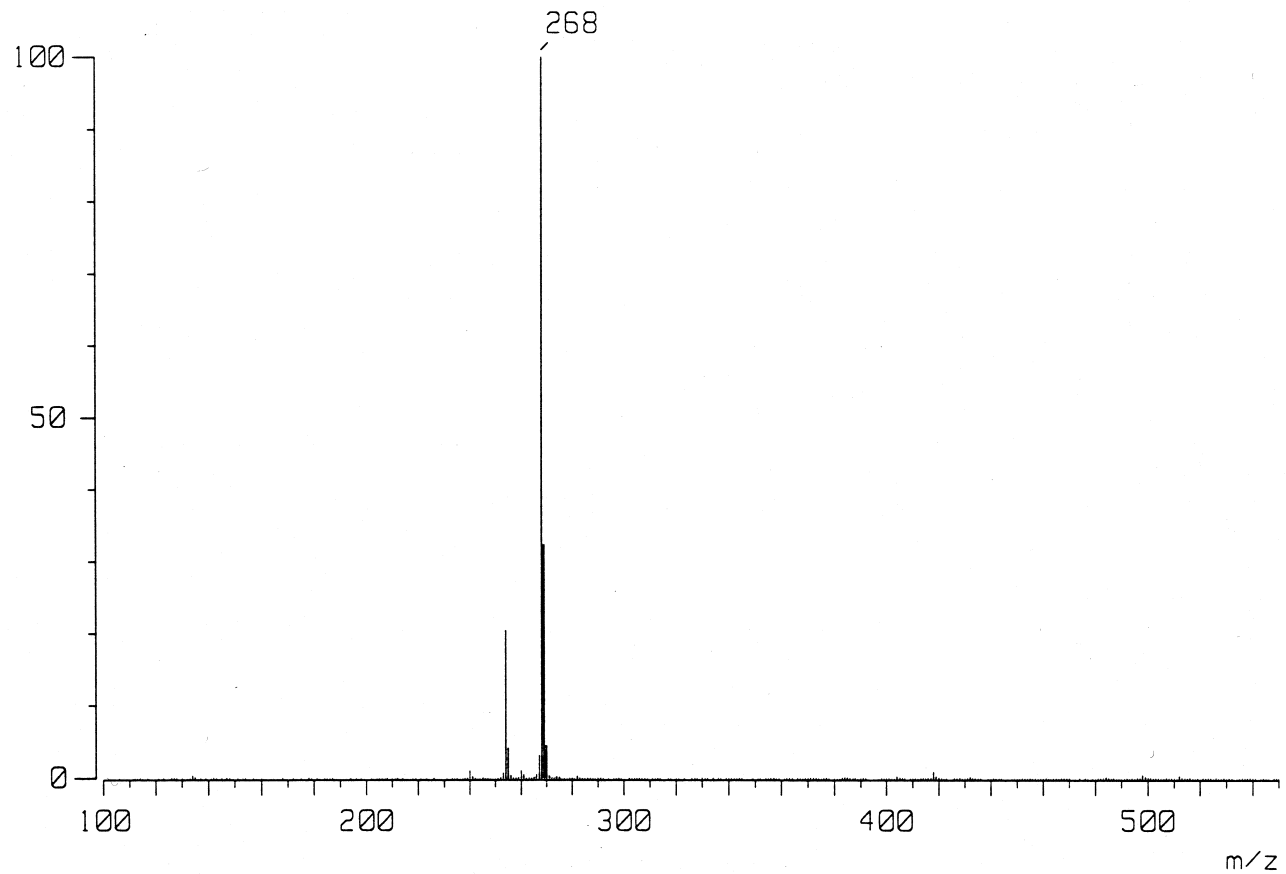

FIG. 5—*FD mass spectrum of Basic Yellow 2.*

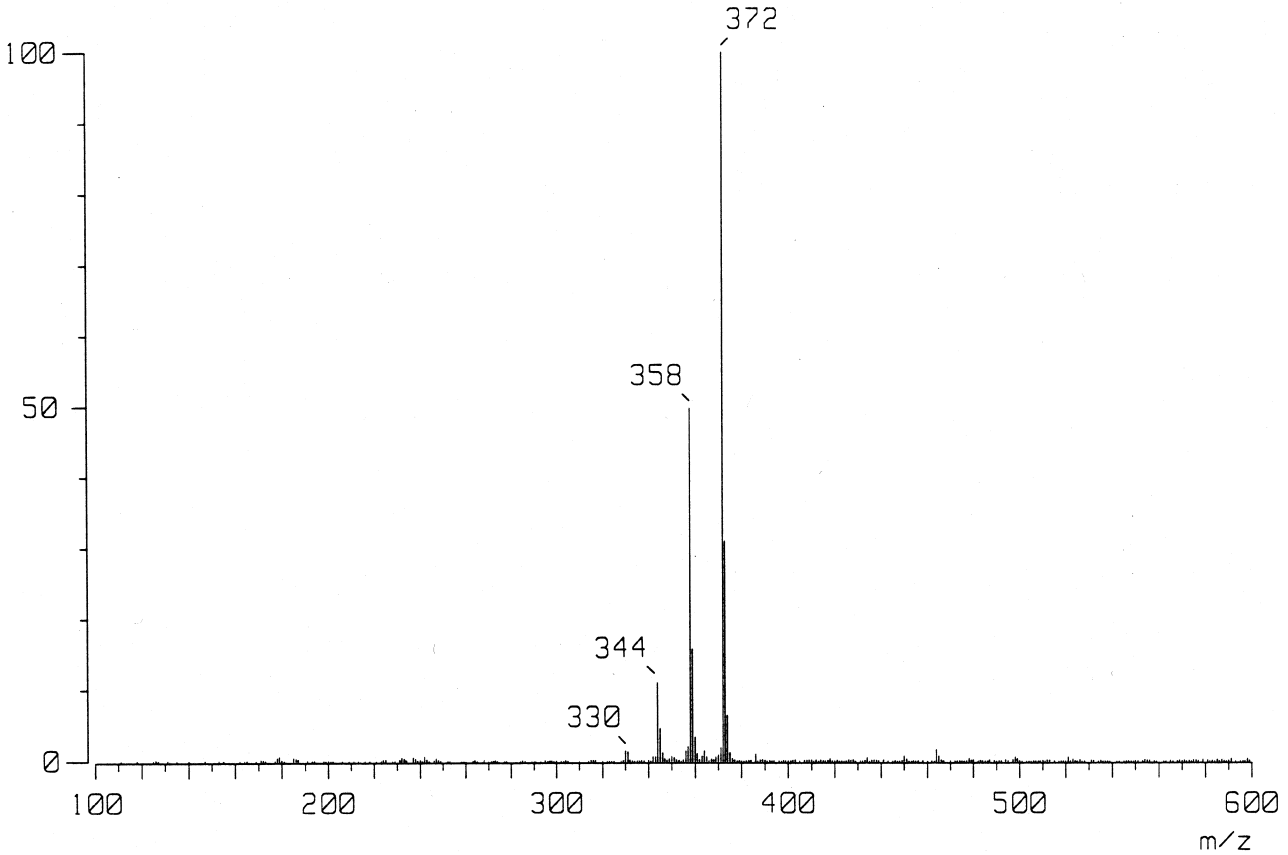

FIG. 6—*FD mass spectrum of Basic Violet 1.*

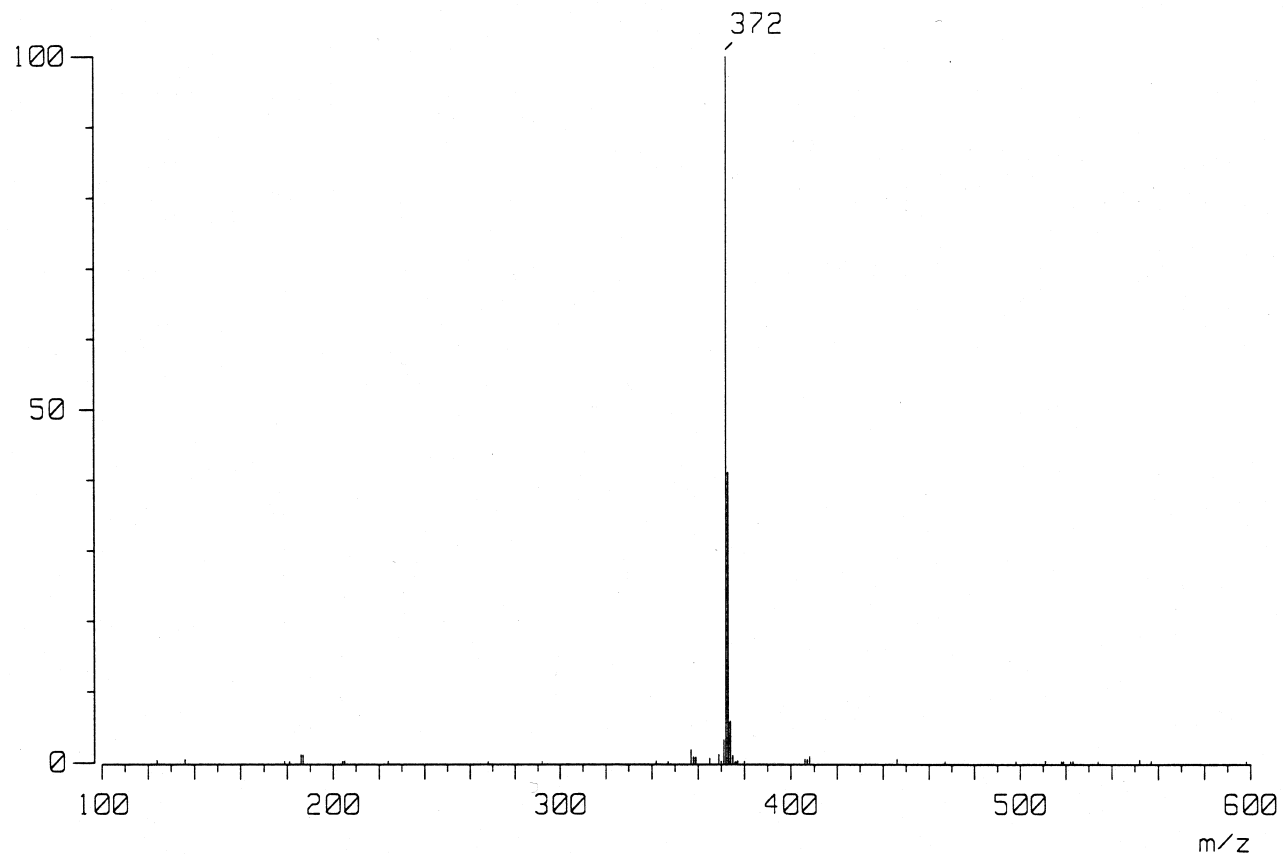

FIG. 7—*FD mass spectrum of Basic Violet 3.*

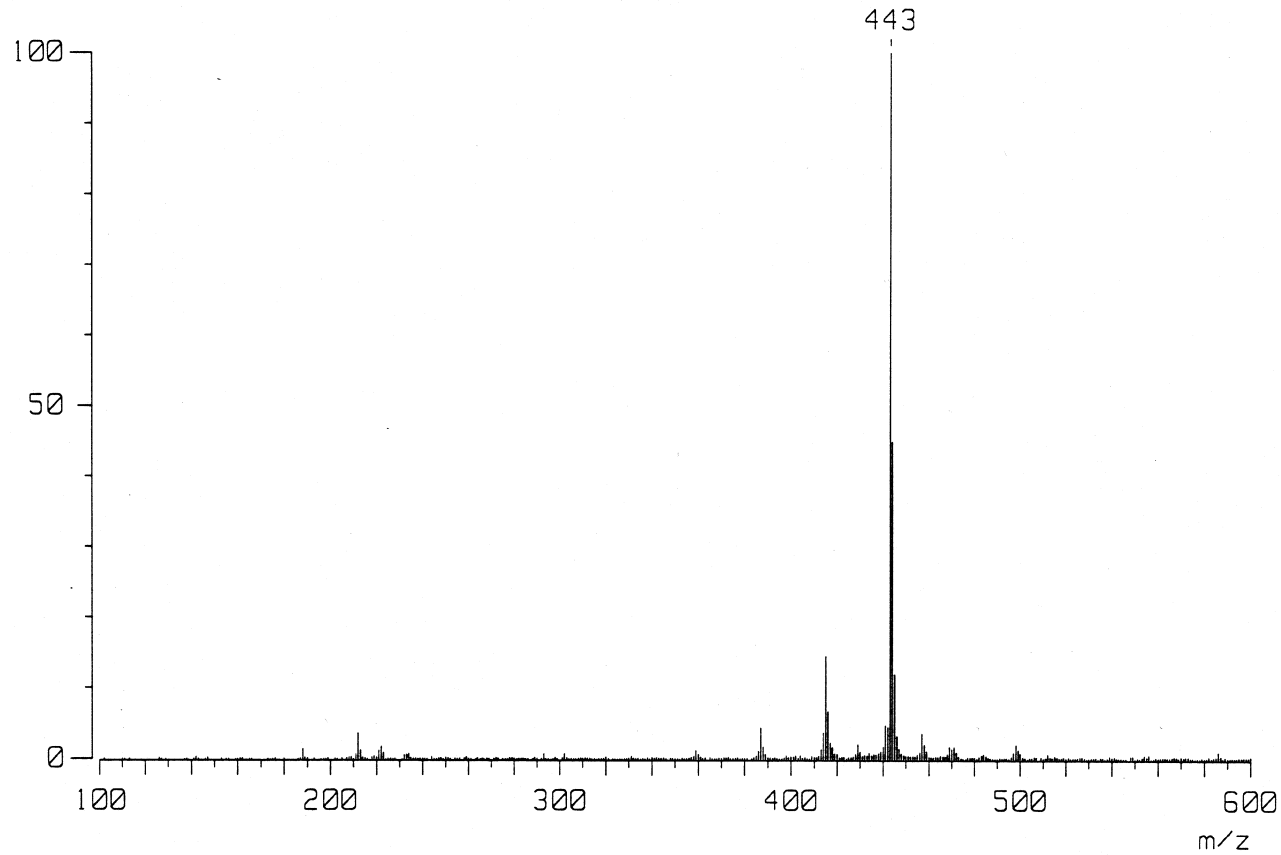

FIG. 8—*FD mass spectrum of Basic Violet 10.*

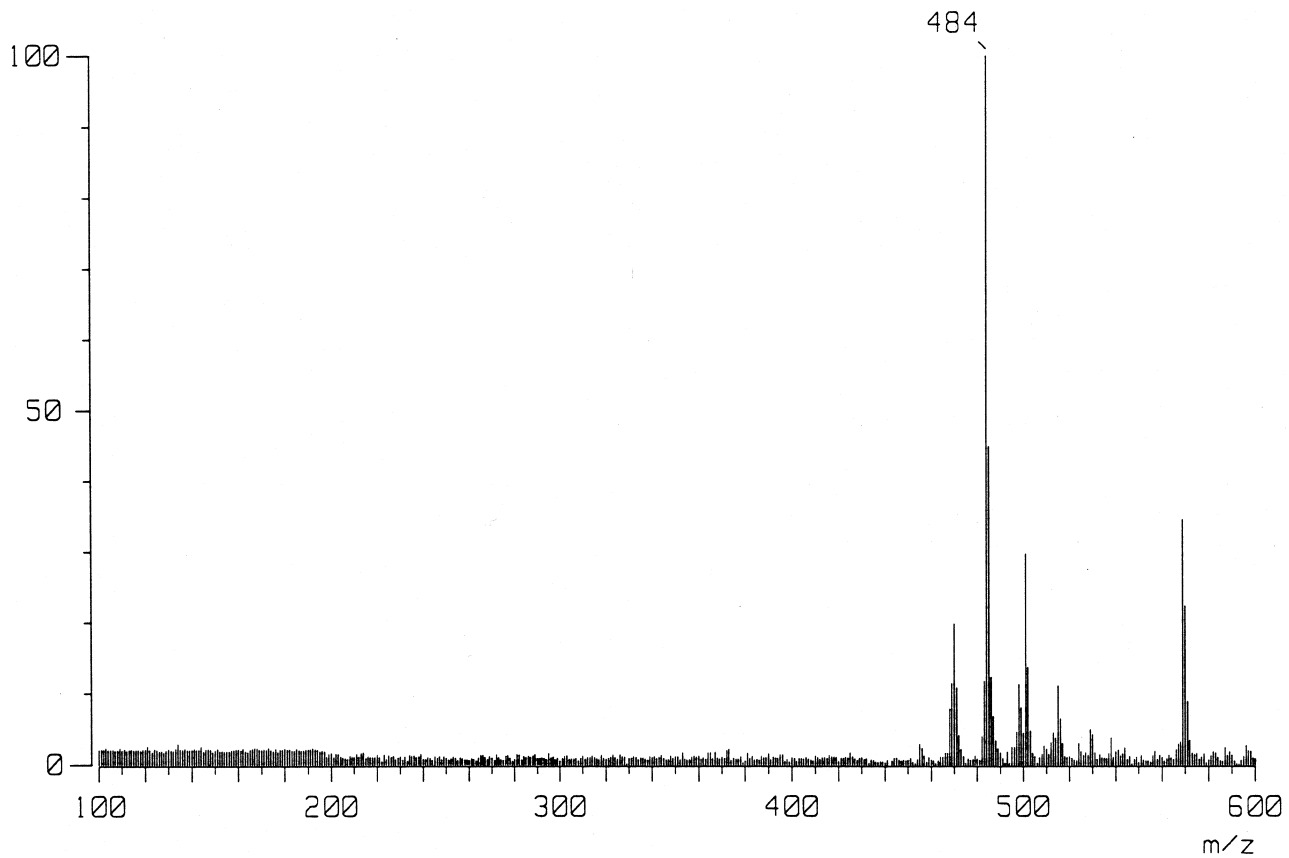

FIG. 9—*FD mass spectrum of Solvent Blue 2.*

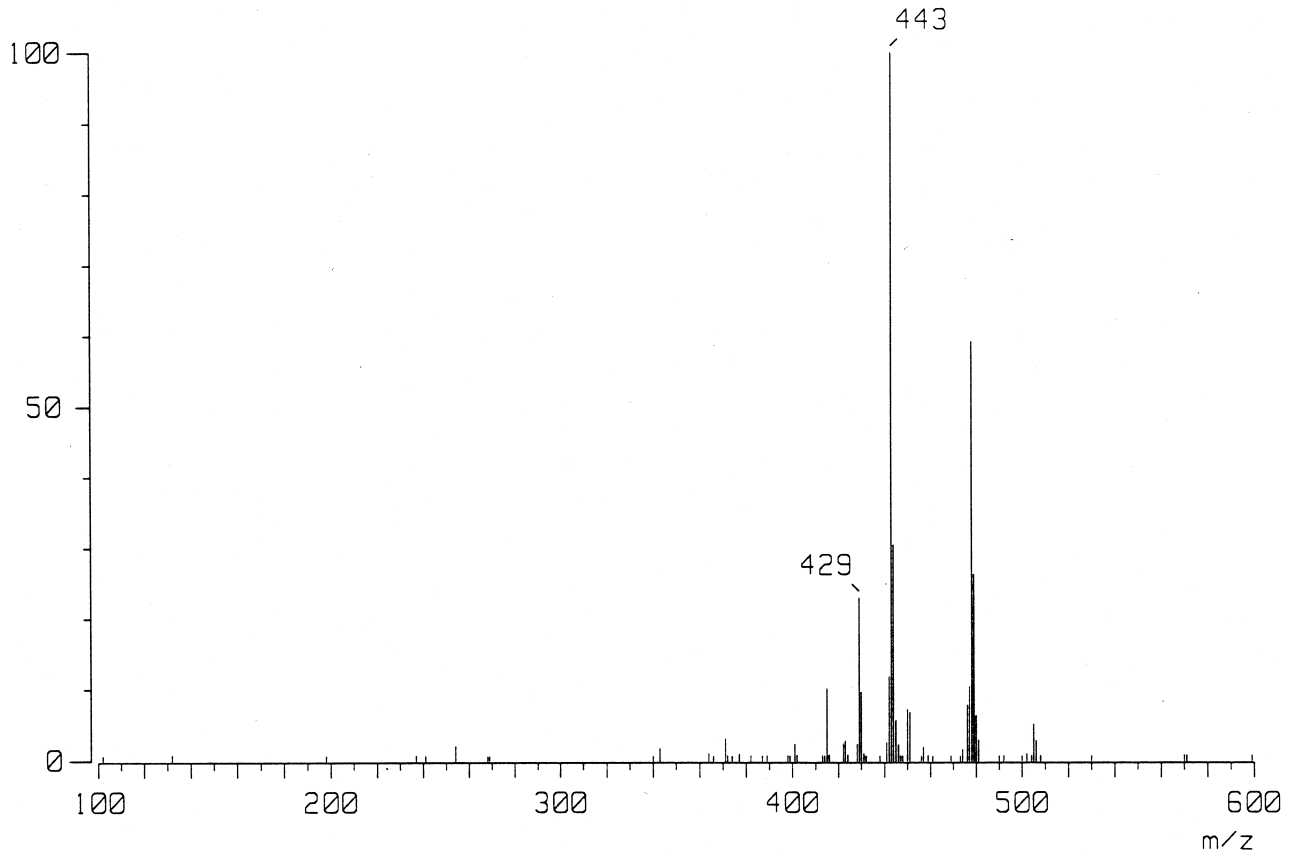

FIG. 10—*FD mass spectrum of black ballpoint pen ink A.*

TABLE 1—*Results of FD mass spectrometry of black ballpoint pen inks.*

Ions Observed	Manufacturer*						
	Black-A	Black-B	Black-C	Black-D	Black-E	Black-F	Black-G
484				+			
478†	+						
443	+						
429	+						
386			+				
372		+	+	+	+		+
358		+	+	+	+		+
344		+	+	+	+		+
340†		+	+		+		
268				+			
Type	I	II	III	IV	II	V	VI

* + = Ion detected, A to G describe the manufacturer.
† = Origin unknown.

Red Ballpoint Pen Inks—The FD mass spectrum of a typical red ballpoint pen ink is shown in Fig. 12. The m/z 429, 268, and 443 ions correspond to the molecular ions of Basic Red 1:1, Basic Yellow 2, and Basic Red 1, respectively. The red ballpoint pen inks from the seven manufacturers were analyzed and the ions detected are summarized in Table 3. The red ballpoint pen inks were classified into six types (Type I~VI).

Some problems associated with our method are described as follows. The length of the ink line used in these analyses was 1 mm because sampling is physically difficult when a length of less than 1 mm is used. Also, it should be noted that Basic Violet 10 and Basic Red 1, which have the same molecular weight but different chemical composition (see Fig. 1) can not be distinguished by detection of the molecular ion. However, these inks can be distinguished due to the spectral signatures of other ions present in these inks. Creating a database of such products could help to identify the pen's manufacturer.

Next, the characteristics and advantages of our method are de-

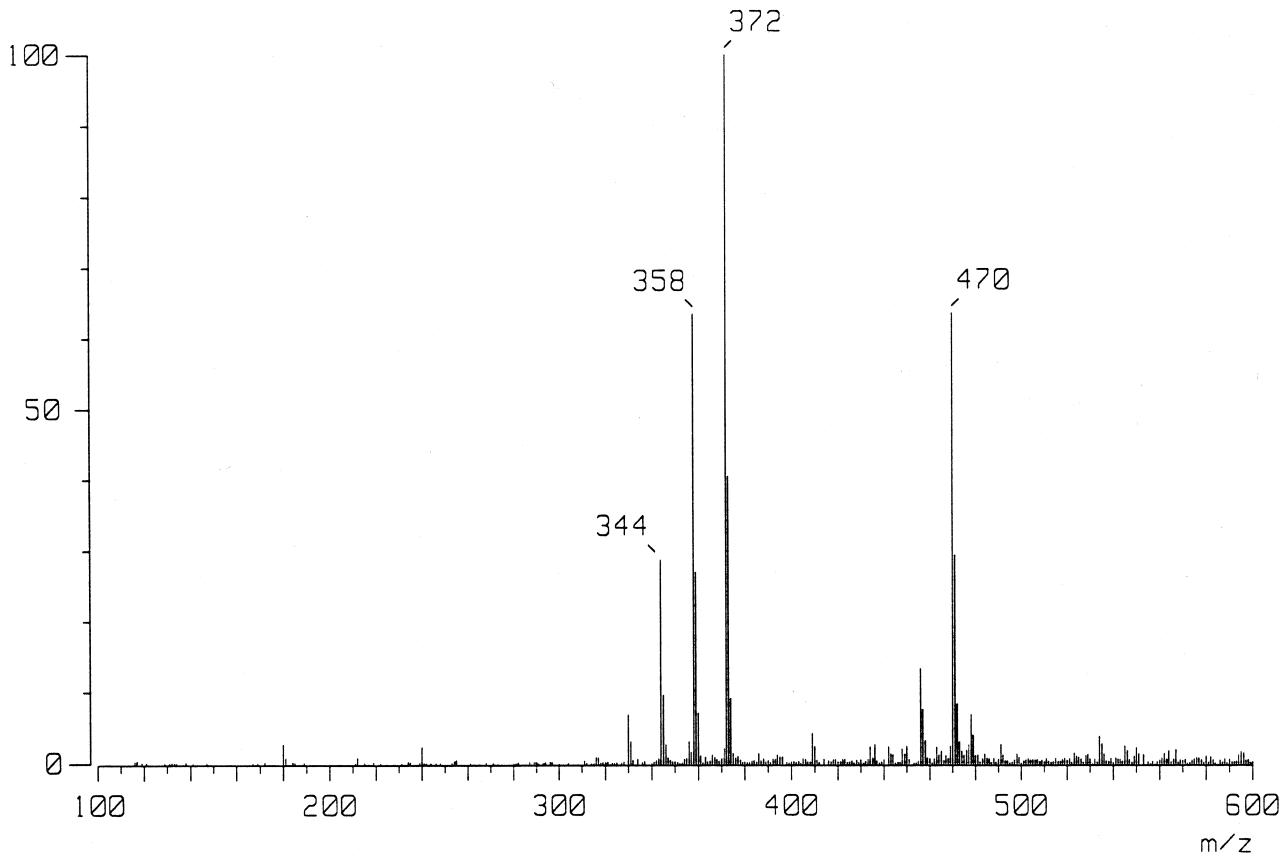

FIG. 11—*FD mass spectrum of blue ballpoint pen ink C.*

TABLE 2—*Results of FD mass spectrometry of blue ballpoint pen inks.*

Ions Observed	Manufacturer*						
	Blue-A	Blue-B	Blue-C	Blue-D	Blue-E	Blue-F	Blue-G
498				+			+
484				+			+
478†					+		
470		+	+	+		+	+
372	+	+	+	+	+	+	
358	+	+	+	+	+	+	
348†		+				+	
344	+	+	+	+	+	+	
320†		+				+	
Type	I	II	III	IV	V	II	VI

* + = Ion detected, A to G describe the manufacturer.
† = Origin unknown.

scribed. A database has already been constructed for FTIR (8) and used successfully to identify the manufacturer of ballpoint pens. However, identification is difficult when the sample is not in the database. Using the FDMS method, identification of the basic dye is possible by means of the mass number of the molecular ion detected. Even if there were no FDMS database, the FDMS method can effectively specify a dye based on the mass number thus providing effective identification of the forensic sample. Furthermore, our FDMS method of analyzing the basic dyes in ballpoint pen ink can be used without the need for any chromatographic sample preparation. FDMS is thus a simple and rapid method for analyzing ballpoint pen ink.

Analysis of Forensic Samples

Our laboratory was commissioned to provide an expert opinion in a case involving ballpoint pen ink. Samples for the examination were a document written with blue ballpoint pen ink and a

specific blue ballpoint pen as a reference. The purpose of the request was to determine whether the ink on the document and that of the reference were of the same origin. The results of the examination by our method indicated that the ink in the document and reference resembled closely, because the same ions were detected with equal relative intensity of each ions in both samples, as shown in Fig. 13. As the ink in the document was also same as the reference in other examinations, we decided that they were identical in this case.

In this commissioned case, the pen was of foreign origin, and because our database consisted of only Japanese ballpoint pen inks there was no similar pen in the database. However, the m/z 372 ($M^+ + 14$), 358(M^+), and 344($M^+ - 14$) ions derived from Basic Violet 1 were detected. Without a database or known reference sample, it becomes necessary to obtain product information directly from each manufacturer that uses Basic Violet 1 dye. The ready availability of such data could facilitate the speed and efficiency of forensic investigations.

^{1}H-NMR Spectra of Basic Violet 3 and Basic Violet 1

Basic Violet 3 ($CDCl_3$): δ 3.28 (18H, s, $NCH_3\times6$), 6.86 (6H, d, J=9Hz, aromatic-H), 7.32 (6H, d, J=9Hz, aromatic-H). Basic Violet 1 (DMSO-d_6): δ 3.19 (18H, s, $NCH_3\times6$), 6.98 (6H, d, J=9Hz,

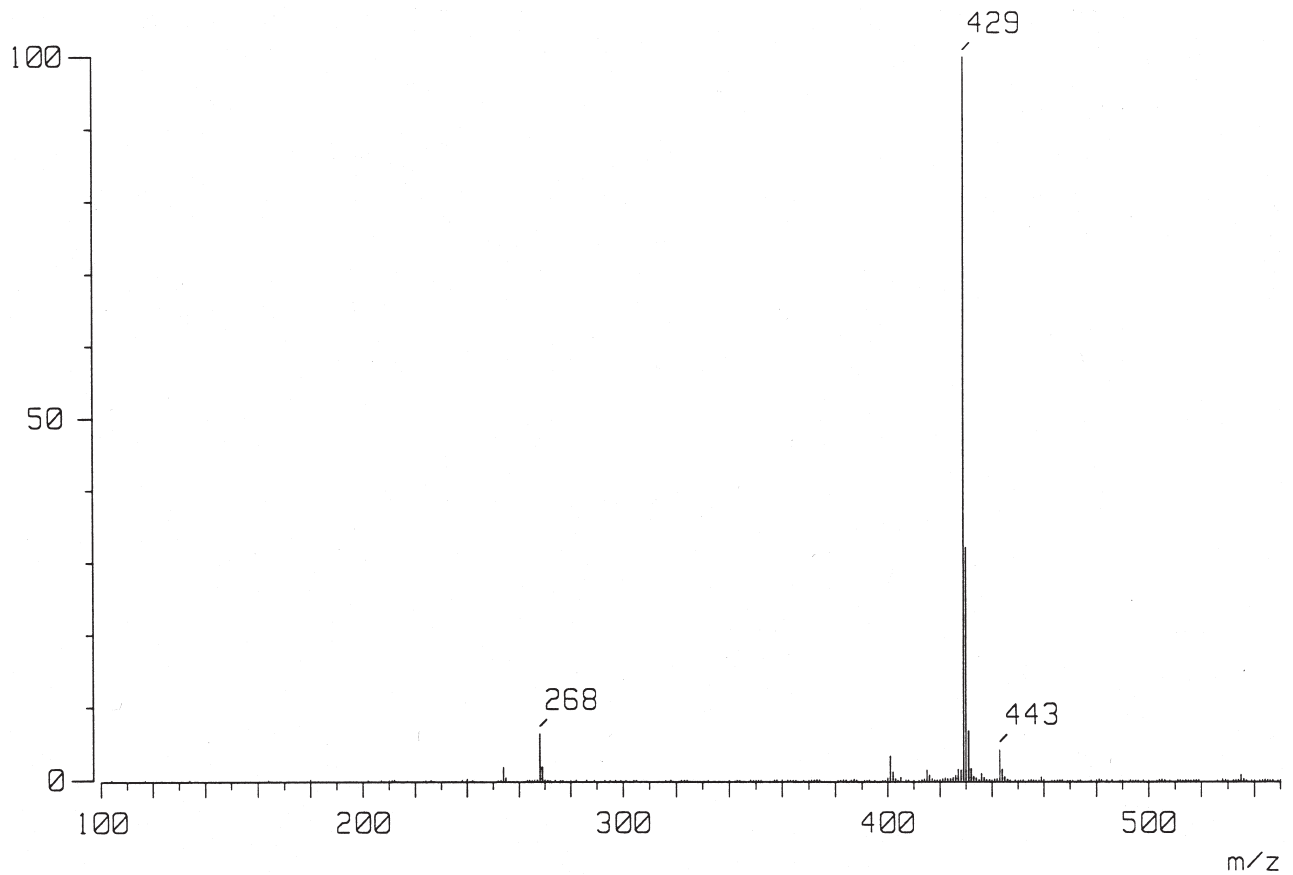

FIG. 12—*FD mass spectrum of red ballpoint pen ink E.*

TABLE 3—*Results of FD mass spectrometry of red ballpoint pen inks.*

Ions Observed	Manufacturer*						
	Red-A	Red-B	Red-C	Red-D	Red-E	Red-F	Red-G
443	+	+	+	+	+	+	+
429		+	+		+	+	
356†			+				
340†		+					
268	+		+		+		
Type	I	II	III	IV	V	VI	IV

* + = Ion detected, A to G describe the manufacturer.
† = Origin unknown.

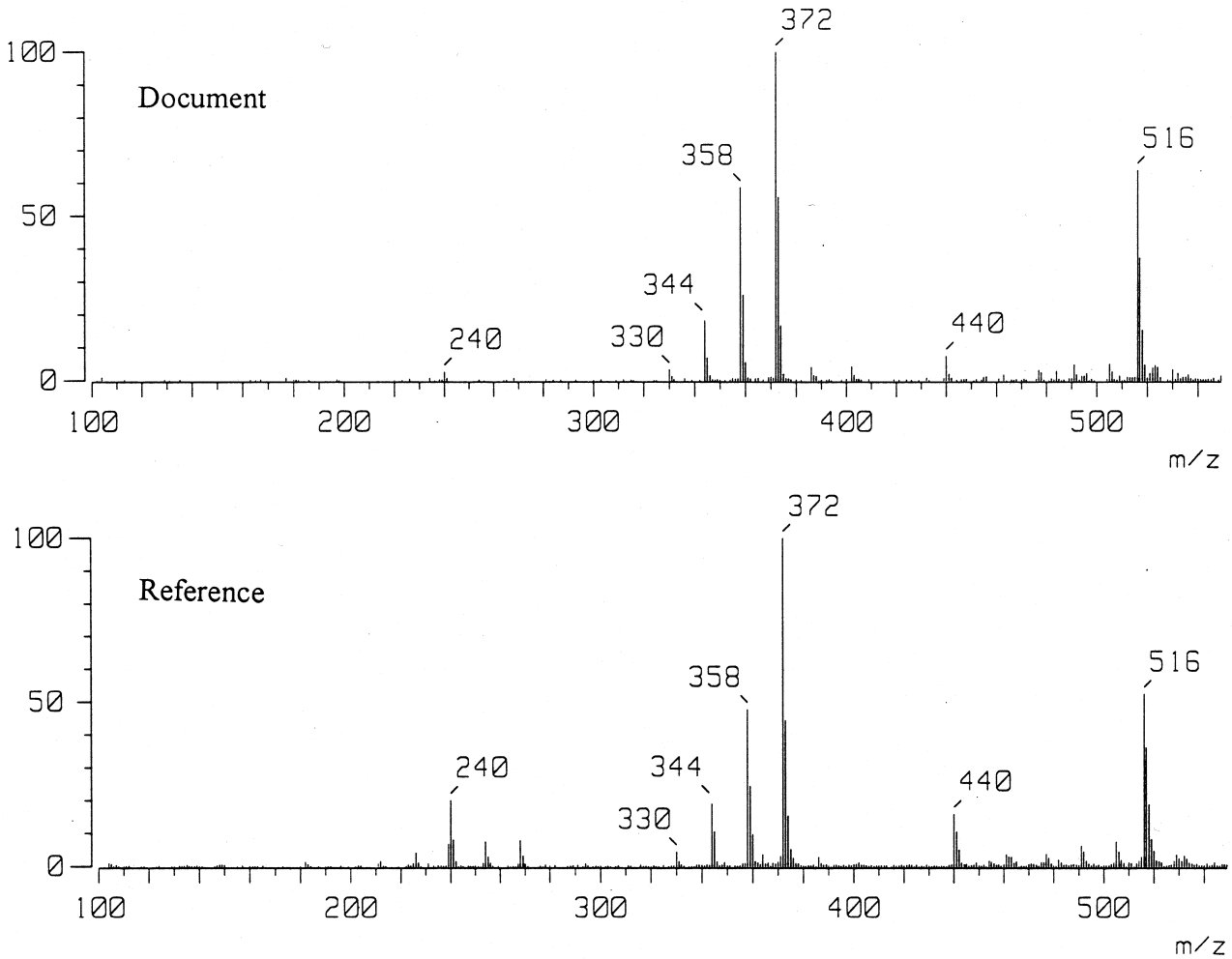

FIG. 13—*FD mass spectrum of document and reference. Document: letters written with blue ballpoint pen ink. Reference: a specific blue ballpoint pen.*

aromatic-H), 7.26 (6H, d, J=9Hz, aromatic-H), originated from Basic Violet 3; δ 2.90 (3H, d, J=4Hz, NHCH_3), 3.18 (12H, s, NCH_3×4), 6.83 (2H, d, J=9Hz, aromatic-H), 6.96 (4H, d, J=9Hz, aromatic-H), 7.23 (2H, d, J=9Hz, aromatic-H), 7.25 (4H, d, J=9Hz, aromatic-H), 8.25 (1H, br, $NHCH_3$), originated from Basic Violet 1. ^{1}H-NMR spectra were recorded with a Varian XL-400 spectrometer.

Conclusion

The results of this study suggest that FDMS can serve as a valuable tool for analyzing ballpoint pen ink. The basic dyes used in these inks have a non-volatile character and this property makes it difficult to analyze them by electron impact and chemical ionization. Using the FDMS method, it is possible to estimate the manufacture based on the molecular ions and specify a dye from the mass number. It was further clarified by our method that ballpoint pen ink is constituted from several kinds of dyes. Therefore, it is possible to distinguish whether the ink in different writing samples is the same or not. Making a database of such ink products could facilitate identification of the pen's manufacturer. An ink line 1 mm in length was used for the extraction and is sufficient for analysis.

This method was applied in an actual forensic case, and afforded valuable results concerning the writing sample.

Acknowledgments

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