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Evaluation of Desorption/Ionization Mass Spectrometric Methods in the Forensic Applications of the Analysis of Inks on Paper*

ABSTRACT: Fast atom bombardment and laser desorption mass spectrometry (LDMS) provide molecular level information concerning an ink's composition. Two ink-jet printer inks, Ink A containing the cationic dye Methyl Violet 2B, and Ink B containing the anionic dye, Solvent Black, were studied. Both positive and negative ion detection modes of the mass spectrometer were used. LD may be used for the analysis of inks on paper. Once on paper, the ink's solvent system has evaporated, leaving mainly the dyes behind, which are detected using LDMS. An ink fades with time, indicating that the dyes are degrading. Preliminary results from an accelerated aging study of ballpoint pen ink using UV irradiation confirm that dye degradation products are formed. The degradation chemistry follows an oxidative demethylation process for which all products formed are detected using LDMS. Results suggest that LDMS may be developed to determine the relative age of inks.

KEYWORDS: forensic science, questioned documents, ballpoint pen ink, accelerated aging, mass spectrometry

> "The ability to determine when a document was written would rate as one of the major breakthroughs in forensic science, having a significant impact on the detection of all kinds of fraud. This would result in a corresponding financial benefit to both State and Federal administrations" (1).

Two desorption/ionization (D/I) mass spectrometry methods, fast atom bombardment (FAB), and laser desorption (LD), are evaluated for the direct analysis of inks and dyes on paper. Both methods are being considered here as tools to determine the composition and age of ink on a document. Questioned document examiners are asked to provide information on many aspects of written and printed inks on paper (2,3). In a court case challenging hospital records, for example, questions may arise concerning whether two entries are from a common origin (the same pen). More difficult questions may be related to the age of an entry. This may require both an identification of the type/origin of the ink, and the length of time that it has been on the record. In the past few decades, the focus of document verification has changed since many challenged documents, such as wills, are no longer hand written. Questions may relate to whether a document was printed using a particular laser or ink-jet printer, or whether the document is an original or a photocopy. This makes the work of document examiners much more challenging. While it is relatively easy to determine the major components in a ball point pen ink, laser printer inks are much more complex and are patent protected.

Analytical instrumentation has been used in the analysis of ink on paper (4,5). Methods such as gas chromatography (GC), liquid chromatography, GC-mass spectrometry (MS), thin layer chromatography, X-Ray fluorescence, and a variety of spectroscopic tools are commonly used to determine an ink's composition. Frequently, measurements used to date ink samples are experimentally simple and do not require complex instrumentation (6). These include ion migration tests (4,6), and a variety of extraction-based methods (4–8,20,21).

Mass spectrometry has previously been used in the analysis of ink (9,10). A mass spectrometer is a very powerful detector following separation by GC. In the GC-MS experiment, volatile components of an ink sample are separated, then ionized using electron impact ionization (EI) and subsequently analyzed by the mass spectrometer. D/I methods that are used with mass spectrometry have the advantage of generating ions for MS analysis from nonvolatile/thermally labile analytes. Currently there are a number of D/I methods available. These are summarized in Table I. For example, field desorption (FD) can be used to generate ions from analyte molecules with molecular weights greater than 1000 (11). In this method, analyte molecules are deposited onto a FD "emitter," which employs a carbon surface. When the surface is heated in the presence of a high electric field, ions can be generated from the analyte. FD has been used very recently for the analysis of ballpoint pen inks (12). Secondary ion mass spectrometry (SIMS) and FAB are two very similar techniques (13). In a SIMS experiment, the analyte is deposited onto a metal surface that is inserted into the ion source of the mass spectrometer. This target is continuously bombarded with ions having several keV of kinetic energy. Secondary ions representative of species on the target surface are generated and analyzed. In the FAB experiment, the analyte is dissolved in a liquid matrix such as glycerol. This viscous solution is deposited on a metal surface, and inserted into the ion source of the mass spectrometer. This target is continuously bombarded using fast (keV) Xe atoms, typically. Both are used with magnetic sector mass analyzers. We note that both FAB and SIMS have been used to obtain spectra of nonvolatile organic dyes (14–16), and there has been one report of using SIMS to analyze colorants on paper (17). Matrix-assisted laser desorption/ionization (MALDI) (18) and LD (19) are very similar experiments, differing only in the presence of a crys-

TABLE 1—*Desorption/ionization methods used in mass spectrometry.*

Method	Analyte Form	Mechanism	Mass Analyzer	Ionization Method
Field Desorption (FD)	Adsorbed on a carbon surface	Thermal excitation and electric-field induced emission	Magnetic Sector	Continuous
Secondary Ion Mass Spectrometry (SIMS)	Adsorbed on a metal surface	Fast ions collide with the surface and deposit energy	Magnetic Sector	Continuous
Fast Atom Bombardment (FAB)	Dissolved in a liquid matrix	Fast ions collide with the target and deposit energy	Magnetic Sector	Continuous
Matrix Assisted Laser Desorption/Ionization (MALDI)	Embedded in matrix crystals	Absorb laser light from a pulsed laser	Time of Flight-MS	Pulsed
Laser Desorption (LD)	Adsorbed on a metal surface	Absorb laser light from a pulsed laser	Time of Flight-MS	Pulsed

talline matrix used to absorb the laser radiation in MALDI. In both techniques, a pulsed laser ionizes a solid analyte. The ions generated are separated using time-of-flight mass spectrometry.

In this work, we consider FAB and LD_MS as techniques for the examination of inks. FAB analyses are usually performed using 1 nmol of analyte dissolved in 1 to 2 μL of glycerol, the viscous liquid matrix. Here we will show that inks can be analyzed directly by FAB. In some cases, viscous solvents in the ink serve the role of matrix for the FAB experiment. To directly analyze ink on a paper surface target, several approaches were considered including saturating the paper in a glycerol matrix. However, we found that FAB will generate ions directly from a dry paper target ("dry-FAB"). This approach is used here.

LD_MS was performed on an instrument designed for MALDI MS. In the current MALDI technology, sample plates containing 100 to 400 "wells" are introduced into the instrument. One μL of a sample solution can be placed in a well. The solvent evaporates, leaving a solid sample target in the well for analysis. The planar target is moved, using mechanical X-Y positioning devices so that a pulsed laser can be focused onto various positions. For our purposes, this plate can be easily modified such that a piece of paper containing ink is introduced, and the paper moved so that the laser irradiates one or more locations where ink is present, generating ions for subsequent MS analysis. Thus, FAB-MS and LD_MS are attractive possible tools for the analysis of inks on paper, because they can readily accept planar targets from which ions can be directly generated upon addition of energy, either by bombardment with fast moving particles or using high power laser radiation.

Numerous approaches have been discussed in the literature (3,5,6,20,21) concerning how to determine the age of an ink. In order to test these methods, practical techniques for accelerating the aging process are necessary, so that "2 year old ink on paper" can be generated in the laboratory in less than two years. Thermal approaches to aging (10,22–24) are used extensively, and are usually followed by an extraction-based analysis for age determination. In this work, accelerated aging is achieved using UV radiation (25). This is not a well-defined accelerated aging process; however, this technique does yield dye modifications similar to those which occur naturally over time.

It is important to define what is meant by "ink." In general, pen and printer inks are chemical mixtures that exist in a liquid, gel or solid form. An ink may be water or solvent based, depending on the mixture of dyes or pigments used. Resins, surfactants, and humectants are added to help the ink adhere to the paper and to vary its physical properties according to the surface to which it will be applied (26,27). When an ink is dispensed onto paper, most of the vehicle (solvent system and additives) evaporates or diffuses into the paper, leaving the dye behind. For forensic applications of ink analysis, it may be more appropriate to refer to ink on paper as dye on paper.

Experimental

Laser Desorption Mass Spectrometry

Instrumentation—The PE Biosystems Voyager DE instrument (Framingham, MA) utilizes a pulsed nitrogen laser (337 nm, 3 ns, 3 Hz) and a linear time-of-flight mass spectrometer. The following user-selected parameters were employed: for analysis of the positive (negative) ions formed by LD, the sample plate was held at a voltage of 20,000 V (−15,000 V), an intermediate acceleration grid was held at 94.5% (94.5%) of the plate voltage, and a delay time of 150 ns was used between laser irradiation and ion acceleration. The manufacturer supplies a sample plate that does not contain wells, but is machined such that a polyacrylamide gel can be attached. When paper is taped onto this metal sample plate, and spectra are generated at a rate of 3 Hz, full resolution of the instrument is realized using the conditions cited here. Care must be taken to maintain a flat target.

Calibration—For TOF MS experiments, ion flight times are measured, and m/z values must be computed. To calibrate LD spectra, a known spectrum containing peaks with known m/z values is first obtained. To do so, a saturated solution of CsI (99.9%; Aldrich, Milwaukee, WI) was pipetted onto paper and allowed to dry. Laser irradiation of this target yields positive ions including Cs^+, and ions with the formula $Cs_{n+1}I_n^+$, such as Cs_2I^+. These were used for calibrating the instrument, such that flight times for other ions could be converted into m/z values in the mass spectra generated. Similarly, for neat ink analysis, 2 μL of the same CsI solution were pipetted onto a gold plate containing wells, allowed to dry, and used for generating spectra for calibration.

Analysis of Ink on Paper—Two industrial ink-jet inks, identified here as Ink A and Ink B, were applied to paper using an air brush (Badger Air-Brush Co, Franklin Park, IL, model 250). This method allowed for minimal, uniform sample loading. In preliminary experiments, the ink from a commercially available ballpoint pen was applied to paper by drawing lines across the paper as evenly as possible, covering a 1 in^2 surface area. Minimizing the space between each line ensured that the laser was irradiating dye-covered paper. With experience, the laser could be focused on regular written pen strokes, such as signatures, and spectra obtained. In UV accelerated aging studies, the sample was irradiated using a UV-lamp (254 nm, 760 microwatts/cm^2; UVP Inc., San Gabriel, CA, model UVGL-58) and analyzed at 12 h intervals.

Fast Atom Bombardment Mass Spectrometry

Instrumentation—A JEOL HX 110 (JEOL USA, Peabody, MA) double-focusing magnetic sector mass spectrometer was used to analyze the positive and negative ions formed following bombardment of samples with 10 keV Xe atoms. The FAB experiment uses a direct insertion probe, which introduces into the ion source a planar, metal surface on which the sample is placed.

Procedures—The instrument was calibrated using Ultramark 4000 (PCR Incorporated, Gainesville, FL), a standard calibration compound. Analyses of ink, neat and on paper, were performed. In the first experiment, ink was applied directly to the probe tip, without a matrix. The mass spectrometer was set for mid-field positive ion analysis. Fast atoms were generated from the JEOL fast atom gun using a potential of 12 kV and an emission current of 5 mA. These conditions produce informative spectra for the determination of ink composition. In the second experiment, the ink-on-paper sample (prepared as described in the laser desorption section) was applied to the probe tip using double stick tape. In these dry-FAB experiments, short signal durations were encountered. When a paper sample is introduced and bombarded under standard operating conditions, ions are generated and detected by the mass spectrometer, but only for a period of 3 to 5 s. Much more time is required to optimize instrument parameters and obtain a spectrum. If the flux of fast atoms is decreased, the sample is desorbed more slowly from the target, resulting in more long-lived signals. For this instrument, one way to accomplish this is to defocus the FAB beam. This decreases the number of fast atoms striking the target per unit area per second. While this decreases signal intensity, it allows for the continuous generation of ions for periods of minutes instead of seconds, so that spectra can be obtained. As in the LD experiment, both positive and negative ions can be generated and analyzed in FAB MS. FAB spectra of oleic acid 99% (Aldrich, Milwaukee, WI) were obtained to compare with ink spectra.

Results and Discussion

FAB MS for the Analysis of Ink

FAB MS can be used for the analysis of inks directly. The ability to identify individual ink components has both industrial and forensic applications. Ink formulators are interested in knowing if an ink's components are reacting and, if so, what the products are. Shelf-life studies (aging studies of the bulk ink) are an integral part of the ink formulation process. Mass spectrometry can be used to detect the products of reactions that occur. Ink chemists can use this information to understand which components are limiting their ink's shelf-life. Forensic chemists often face the task of matching ink samples to sources. One may not have had previous experience with a particular ink, therefore, it would be impossible to predict what components could be present in an aged sample. In order for an ink source and a written document to be linked, information on the ink mixture would certainly assist. Also, for more complex samples like ink-jet printer inks, when the composition is unknown, it will be very useful to have information on the ink as well as the components on the printed document.

FAB is a batch method in which, ideally, one spectrum is representative of multiple components. Ideally, all components are desorbed/ionized at the same time. However, since the mass spectrometer is held at a low pressure, the low molecular weight, volatile components can quickly be lost. Fortunately, this process is similar to what would occur naturally due to evaporation when

an ink is applied to paper. Thus, FAB MS is not expected to identify every component. Fortunately, the dyes used in this study are not volatile, and are dissolved in viscous solvents, which are similar in nature to the glycerol matrix typically used in FAB experiments. Thus, the inks are good targets for this technique.

Figure 1 shows two portions of the positive ion FAB spectrum of Ink A. From this spectrum, a number of components were identified. The region of the spectrum below m/z 300 (Fig. 1*a*) suggests the presence of oleic acid, $C_{17}H_{33}COOH$. In positive ion FAB, neutral analyte molecules are frequently desorbed in protonated form-the neutral molecule M is generated in the gas phase as a protonated molecule, $[M+H]^+$. The peak at m/z 283 in the spectrum represents these ions. The protonated molecule efficiently loses water to form a major peak at m/z 265. Lower mass peaks at m/z 55, 69, 83, etc. are indicative of the hydrocarbon portion of oleic acid. Similar peaks are observed in El spectra of alkanes. A FAB spectrum of pure oleic acid (not shown) was obtained, which matches this portion of the spectrum. Oleic acid is a viscous organic acid, which is the primary solvent of Ink A's vehicle.

Figure 1*b* represents a higher mass region of the positive ion FAB spectrum of Ink A, which indicates that one of the dye components is Methyl Violet 2B. The structure is shown in Fig. 2. Methyl Violet 2B is a cationic dye consisting of three phenyl groups, with five methyl groups attached to three nitrogens. The dye is introduced as a salt (C^+A^-). The cation is desorbed directly from the sample, and C^+ is observed in the spectrum (m/z 358). Dyes are frequently mixtures. For this particular dye, the hexamethylated form is more abundant than the pentamethylated form. This becomes evident when examining the ink's spectrum. The base peak (largest peak) in Fig. 1*b* is seen at m/z 372, which corresponds to the hexamethylated structure, whereas the peak at m/z 358 represents the pentamethyl form of the molecule. The homolog with four methyl groups yields the peak at m/z 344. The peak at m/z 368 remains unassigned. The nature of this dye will be discussed in more detail in a following section. Key at this point is the fact that the peaks in the region of the spectrum shown in Fig. 1*b* are indicative of the presence of this cationic dye, and that ink components can be detected using FAB.

In contrast, Ink B contains a very different dye, Solvent Black. The dye consists of a Cr^{3+} center with two identical ligands, each carrying a 2-charge, attached to it. The structure (shown in Fig. 2) carries an overall negative charge, making it anionic. As with the cationic dye, an anionic dye is introduced as a salt C^+A^-. When detecting negative ions, the dye should be detected as A^-. In contrast to ionic materials, neutral analyte molecules are desorbed in deprotonated form in negative ion FAB, meaning that the neutral molecule M is detected in the gas phase as $[M-H]^-$. Figure 3*a* shows the low mass region of the negative ion FAB spectrum of Ink B. The primary solvent, triethylene glycol, is detected in deprotonated form at m/z 149. In Fig. 3*b*, a higher m/z portion of the same spectrum, the peak at m/z 666 corresponds to the major anionic dye component (A^-), Solvent Black.

The FAB spectra, Figs. 1 and 3, show that components of inks, especially ionic dyes, are easily detected using FAB. Stable aromatic molecular species such as dyes are desorbed/ionized in a single form—yielding a single, intense peak with no fragmentation. In contrast, oleic acid, which is made up mostly of single bonds, fragments extensively.

To evaluate the utility of various D/I methods for this field, the same ink samples were analyzed using LD_MS. As an example, Fig. 4*a* shows the positive ion LD_MS spectrum of Ink A. Only peaks representing the dye are observed. If the spectra shown in
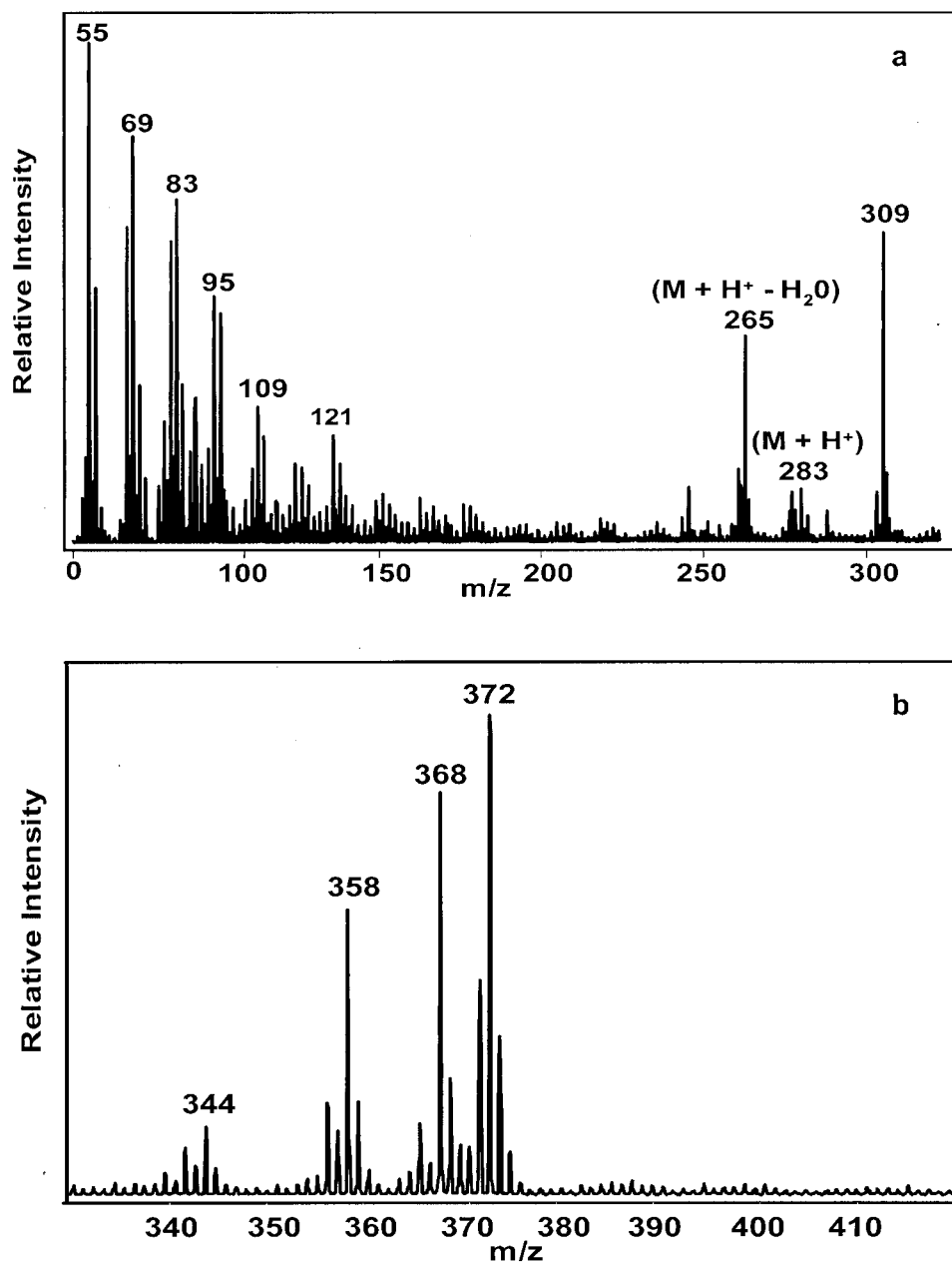
FIG. 1—*The positive ion FAB mass spectrum of neat Ink A: Region (a) shows peaks representing oleic acid and region (b) shows peaks representing Methyl Violet 2B.*

Figs. 1 and 4 are compared, it is clear that more components can be identified using FAB. This is reasonable based on the mechanism of desorption/ionization for these methods. In FAB, the mixture is bombarded with fast atoms and all species present absorb energy, and can be desorbed/ionized. If a species is ionic it will be desorbed directly. If it is neutral, it will be detected if chemistry can occur during the FAB process that will protonate or deprotonate the molecule (resulting in positive or negative ions). In contrast, LD is more of an optical technique. Here, the sample is irradiated with 337 nm light from a nitrogen laser. Only those molecules that absorb light at this wavelength will be affected. In the case of ink, most of the components are transparent at this wavelength; only the dye absorbs and is transformed into gas phase ions. Thus, for mixture analysis of this type, FAB would yield information on a larger number of components. The situation becomes such different when the target for analysis is ink on paper, since dyes become the main component present.

Analysis of Dyes on Paper

While industrial ink chemists would use results from the analysis of bulk ink, forensic chemists would benefit more from the analysis of ink on paper. An important question is related to the sample sizes involved. Is there a sufficient surface concentration of dye deposited on paper during writing or printing to be detected in a FAB or LD experiment? Consider a typical ballpoint pen cartridge, which contains about 0.6 g of ink (27). For the pen we used, the written line was 0.36 mm wide. We assumed that an ink contains

20% dye by weight. In the case of Methyl Violet 2B (molecular weight of 372 g/mol), the ink cartridge would contain 0.3 mmol of dye. Also considering that one ink cartridge can write a line approximately 3000 m long (27), this correlates to about 0.3 mmol/m^2 of sample, as a molar surface coverage per unit area. In a FAB experiment, a nanomole of analyte is typically dissolved in a microliter of a viscous liquid matrix and deposited on the end of a direct insertion probe tip. This correlates to approximately 0.3 mmol/m^2 as an analyte surface coverage, suggesting that there will be enough dye sample present on paper to detect in a FAB experiment. In MALDI MS, picomolar amounts of sample are used, corresponding to a molar surface coverage of 0.3 μmol/m^2; however, in the MALDI experiment, the analyte is not absorbing laser energy directly. Matrix surface concentrations are larger. Considering the fact that laser-based methods have been cited as having extremely low detection limits, in the range of 10^{-18} to 10^{-19} g, it is likely that the surface coverage of dye deposited on paper during writing and printing will be sufficient for direct laser desorption. Based on the ease of analysis and flexibility of the LD MS experiment compared to FAB MS, and the simplicity of the instrumentation, the decision was made to focus on LD_MS, rather than FAB, for the analysis of ink on paper. We note that FAB spectra were successfully obtained, however, short signal durations (see experimental section) made the approach less than ideal.
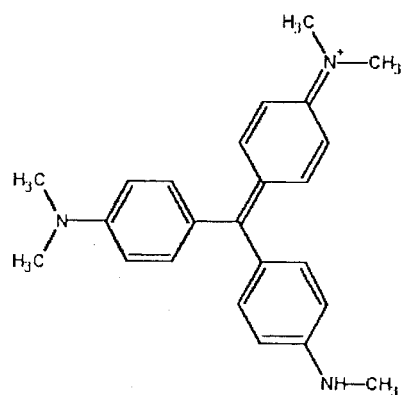
Methyl Violet 2B
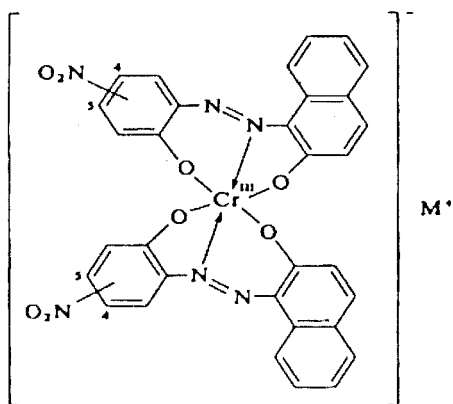
Solvent Black

FIG. 2—*The structures of the cationic dye, Methyl Violet 2B, and the anionic dye, Solvent Black.*

Figure 5a shows a portion of the positive ion LD mass spectrum of Ink A on paper. The peaks shown from m/z 344–372, separated by 14 μ, represent the components of the cationic dye. These are the dominant peaks in the mass spectrum. This is very similar to the FD mass spectrum reported by Sakayanagi et al. (12) for the same dye. To ensure that all of the peaks present in the spectrum are indeed from the ink and not from the paper, both positive and negative ion LD mass spectra were taken of the paper itself. The positive ion LD mass spectrum of the paper substrate used in the analysis of ink on paper and in the accelerated ink aging study, is shown in Fig. 5b. When paper is subjected to UV laser irradiation in this experiment, alkali ions are usually observed as intense peaks at m/z 23 (Na$^+$) and m/z 39 (K$^+$). Two peaks, at m/z 284 and m/z 574 consistently are formed. Their assignments are unknown, but it is clear that they do not represent ink components. These two peaks representing the paper are not always observed when an ink sample is being studied. This may depend on the extent of coverage of the paper by the dye. For example, in the experiment that resulted in the spectrum shown in Fig. 5a, no paper-related peaks were observed. Figure 5c shows a portion of the negative ion LD mass spectrum of Ink B on paper. The peak at m/z 666, the largest peak in the spectrum, shows that Solvent Black can clearly be detected. Many spectra can be generated at high signal-to-noise ratios, indicating that LD_MS can be used for the direct detection and analysis of inks-on-paper, at the surface concentrations typically encountered in written documents. Obviously, for an ink sample, an analyst may not know if an anionic or cationic dye may be present. However, it has been our experience that sufficient ink is present to perform both positive and negative ion LD MS analyses. We estimate that when the laser is focused on a point of a written pen line on paper, more than 600 spectra can be generated before the ink on that site is desorbed completely.

Preliminary Results—Aging Studies

Since LD_MS can directly detect dyes on paper from ink, the decision was made to analyze ink from a ballpoint pen. Over time, ink on paper changes in appearance. This suggests that the chemical composition of the dye molecules is changing. Possibly, the dye could polymerize. If this occurred, the LD mass spectrum of aged ink on paper would show new peaks in the higher mass region. Perhaps, we would see a decrease in the molecular ion peak intensity and the appearance of peaks in the lower mass region indicating that the dye is degrading. If the dye is extremely stable, there is the chance that the spectrum would not change. In an attempt to generate an aged ballpoint pen sample, to compare with a fresh sample, accelerated aging techniques were considered. In the literature, thermal aging (10,22–24) works well and is used extensively when followed by solvent extraction methods. UV irradiation is commonly used in the dye manufacturing industry (29,30) to induce fading, which also occurs with age. We chose UV irradiation as our method of artificial aging, for this demonstration, since it allowed a simple multiplexing of the experiment. Typically, a piece of paper roughly 1 in^2 is placed on the sample plate for ink analysis. The focused nitrogen laser irradiates a very small fraction of this area at any time. Ink from a commercially available black ball point pen containing the dye Methyl Violet 2B was first applied uniformly to the paper. The entire sample was irradiated using a UV lamp for 12 h. A portion was covered and irradiation continued. Irradiation for 12 or more hours results in fading that can be clearly seen. By using masks, an array of UV aged ink on a single piece of paper could be easily generated, introduced as a single sample into the mass
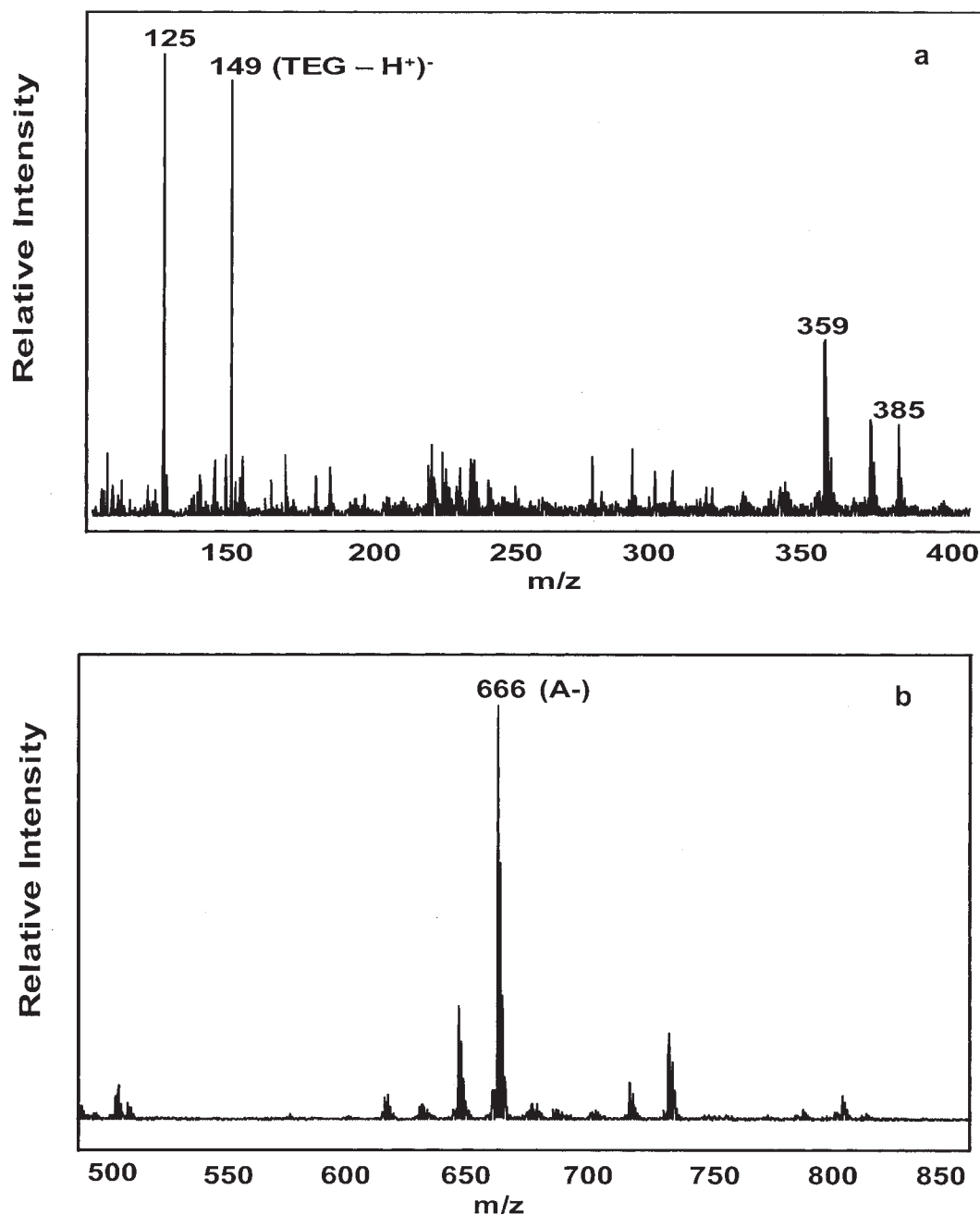
FIG. 3—*The negative ion FAB mass spectrum of neat Ink B: In the low mass region of the spectrum* (a)*, a peak representing triethylene glycol (TEG) is shown. In the higher m/z region of the spectrum* (b)*, the peak at m/z 666 represents the anionic dye Solvent Black.*

spectrometer, and spectra for each region obtained. For this preliminary work, the simplicity of UV aging made it a good choice. We acknowledge that there is currently no accepted irradiation/age correlation for this experiment.

The preliminary UV accelerated aging data are presented in Fig. 6. Positive ion LD mass spectra are shown of the Methyl Violet 2B dye as originally deposited by the ballpoint pen onto paper, and the same portion of the mass spectrum is shown following 12 and 24 h of UV irradiation. After irradiating the sample for 12 h, degradation product peaks are clearly present—a series of peaks separated by 14 μ, with lower m/z values than the major component. The m/z 372 peak remains the base peak. The spectrum shows that six new compounds, lower-mass forms of Methyl Violet 2B, are now in

abundance. Irradiating the sample for another 12 h, causes the initial base peak to further decrease in intensity, such that the degradation product peaks dominate.

When Methyl Violet 2B is reduced in mass by 14 μ, this likely represents the loss of a methyl group—more precisely the replacement of a CH_3-group (15 μ) with a H- atom (1 μ). The peak at m/z 372 corresponds to the hexamethylated form of the dye, as indicated in Fig. 6 as $C^+(Me)_6$. If one —$N(CH_3)_2$ group is converted into —$N(CH_3)(H)$, the new molecular cation, designated as $C^+(Me)_5$, will appear in the mass spectrum at m/z 358. The $C^+(Me)_6$ structure has six methyl groups that can be replaced—if all six react in this way, the lowest mass product would be $C^+(Me)_0$, in which all 6 methyl groups are replaced by H- atoms.

This results in the peak at m/z 288. Thus, the facts that: a loss of 14 corresponds to a methyl/H substitution, the framework of the dye carries up to six methyl groups, and that 6 degradation products are formed, is consistent with this description of the chemistry.

The replacement of methyl groups with H atoms in triarylamine dyes, in their reaction with water molecules, is well known, and is an example of the process of oxidative demethylation. The reactant need not be water—other molecules, including cellulose, are capable of providing the H atoms that replace the methyl groups. The reaction can be photocatalyzed, and can occur in the presence of TiO_2, a common white pigment used in paper manufacturing (31). While UV aging was used just to induce a chemical change in an ink dye on paper, and to show that the change in composition could be detected using LD_MS, we believe that UV accelerated aging has potential in experiments where the dye can be analyzed directly. We have begun to take LD mass spectra of ballpoint pen inks on documents that are 10 to 20 years old, and the same chemistry clearly takes place as part of the natural aging process, with the same oxidative demethylation products being formed. Thus, we are pursuing correlations between UV irradiation times in accelerated aging experiments, and the corresponding actual age of inks. In these UV irradiation studies, we do not consider this as a way of accelerating the kinds of chemical changes that occur in dyes when exposed to sunlight or room light for extended periods of time (fading). Rather, Methyl Violet 2B undergoes a reaction with components of paper, catalyzed by TiO_2, that leads to oxidative demethylation products. This occurs even if the sample is never exposed to light. It is not our contention that UV irradiation makes the ink fade faster, but it is our observation that UV irradiation accelerates this particular chemistry. We attempt to make this distinction here, since changes occur at a molecular level with UV irradiation, even though no visible changes to the written line (fading) are seen.

Conclusion

New D/I techniques in mass spectrometry offer the opportunity to sample molecules directly from planar surfaces, making them an attractive possibility for use in document examination. Certainly, mass spectrometers are expensive relative to the other
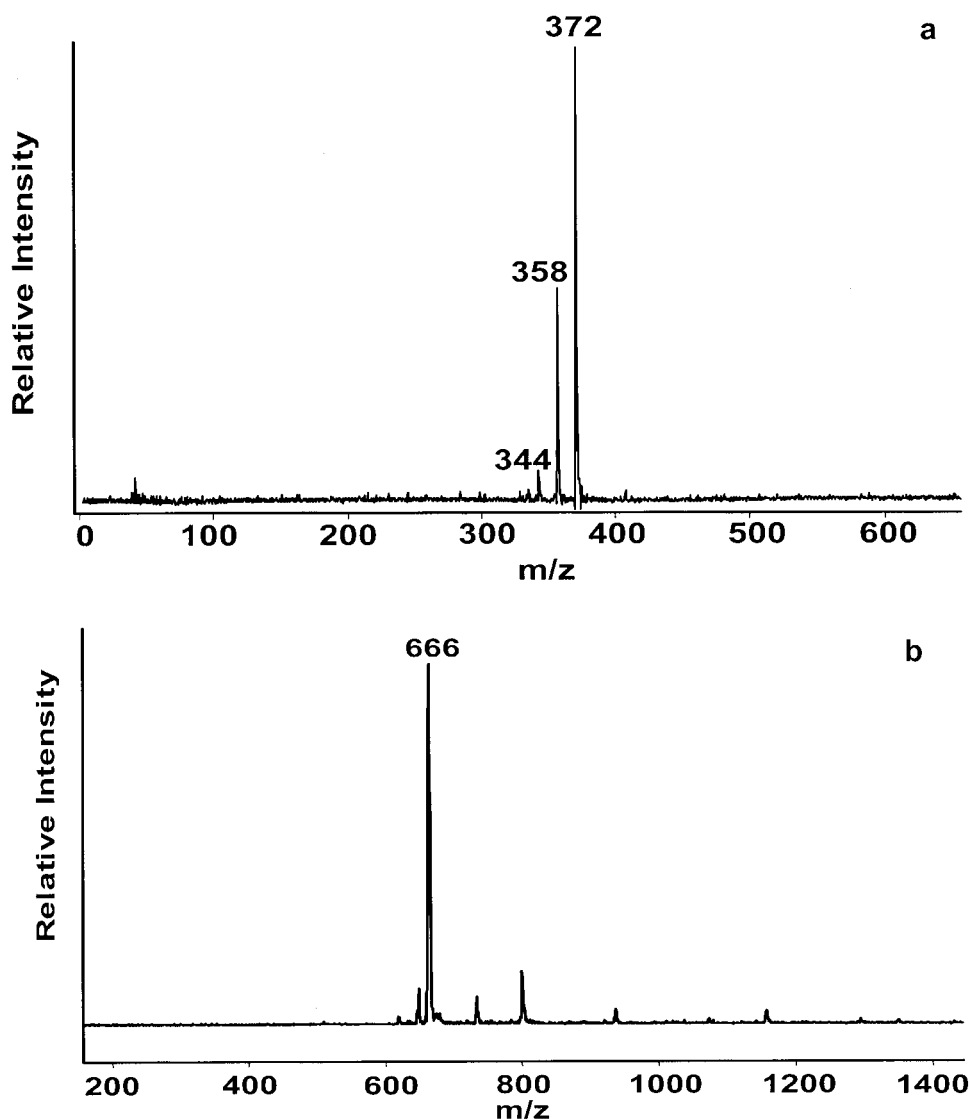

FIG. 4—*Laser Desorption Mass Spectra:* (a) *The positive ion spectrum of neat Ink A and* (b) *the negative ion spectrum of neat Ink B.*
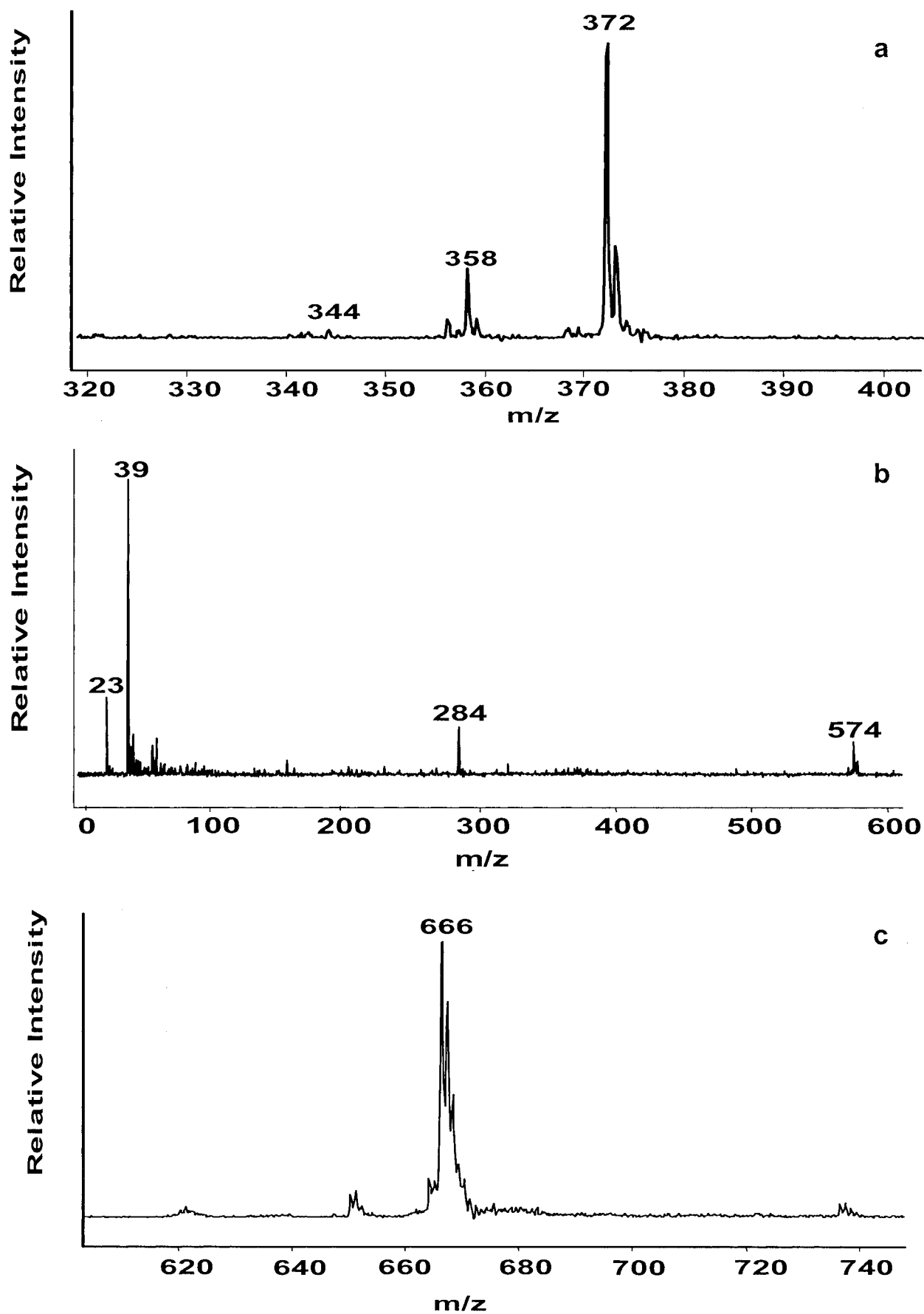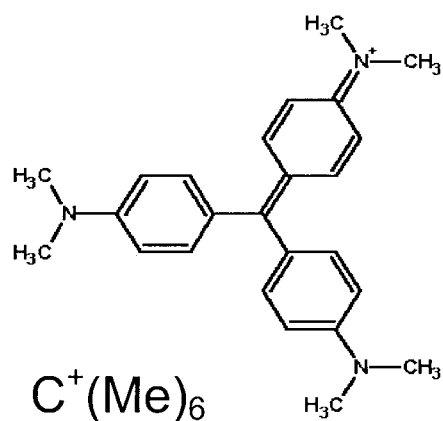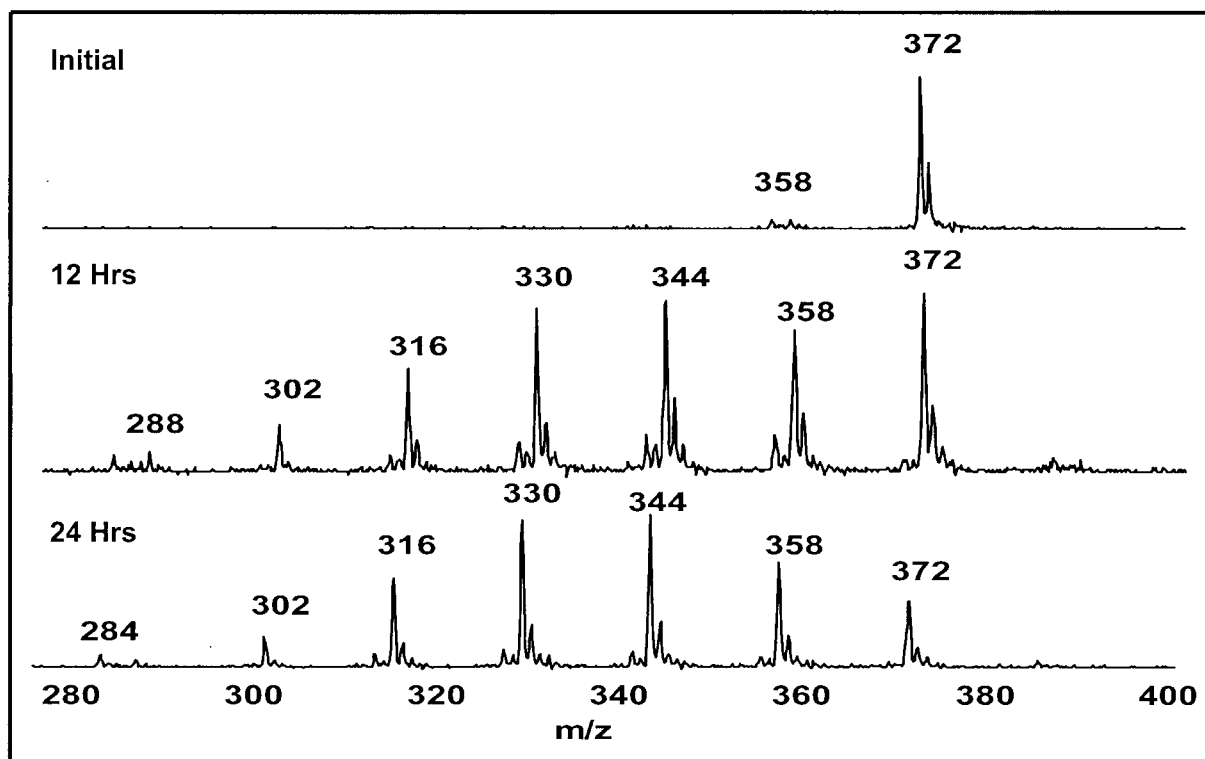
FIG. 5—*The positive ion LD mass spectra of:* (a) *Ink A on paper and* (b) *Hammermill Fore DP paper, and* (c) *the negative ion LD mass spectrum of Ink B on paper.*

m/z	structure
372	$C^+(Me)_6$
358	$C^+(Me)_5$
344	$C^+(Me)_4$
330	$C^+(Me)_3$
316	$C^+(Me)_2$
302	$C^+(Me)_1$
288	$C^+(Me)_0$

FIG. 6—*Preliminary UV accelerated aging study using black ballpoint pen ink. Positive ion laser desorption spectra are shown for the ink when it is first applied to the paper, and following 12 and 24 h of UV irradiation. The peak at m/z 284 is from the paper, not the ink (see Fig. 5b). The m/z values of the UV irradiation products, and their corresponding structures, for Methyl Violet 2B, are listed, and are discussed in the text.*

tools commonly used in such work. However, as is shown here, FAB and LD provide the opportunities to directly analyze dyes on paper. The chemical composition of these dyes change with time, and their reaction products can be detected as well. This direct analysis, at the molecular level, offers chemical information on the ink aging process. With a pulsed UV laser, dye molecules can be desorbed after being on paper for more than 30 years, even though it is generally acknowledged that, based on extraction methods, it is more difficult to remove a dye from paper as it ages (5).

Both FAB and LD are shown to be useful tools for ink and dye analysis. If aging studies can be performed by characterizing the dye and dye degradation products alone, then LD will be the preferred method. If other components on the paper such as surfactants become important, FAB MS may be more useful and versatile.

Finally, a comment should be made on whether LD_MS is a destructive technique. For our work, portions of documents were introduced into the mass spectrometer. Certainly, instruments could be constructed that would allow for larger format samples to be introduced—such as entire documents. The laser used can focus to a

spot (0.03 cm^2) with the dimension of a single pen stroke. In the laser desorption process, molecules are removed from the surface and thus it is a destructive method. However, very small amounts of material are ablated with each laser pulse (each of which is only 2×10^{-12} sec in duration). To date, we have not seen any visual change in laser irradiated areas of ink on paper following generation of a laser desorption mass spectrum. Thus, while molecules are lost from the document, the experiment may be done without visible damage or alteration.

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