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The Direct Detection and Identification of Staining Dyes from Security Inks in the Presence of Other Colorants, on Currency and Fabrics, by Laser Desorption Mass Spectrometry

ABSTRACT: Laser desorption mass spectrometry (LDMS) is useful for the direct desorption and MS analysis of dyes off materials such as paper. Here it is shown that staining dyes, produced by currency degradation devices, such as those used by financial institutions or armored transport companies, can be detected by LDMS. These staining dye packs are commonly used in bank security programs to deter theft or unauthorized removal of currency from teller stations or from ATM cash cassettes. Working automatically, these technologies release a security dye to degrade the surface of the notes and possibly mark the assailant involved in the attack. These dyes can be characterized and identified directly from paper currency, and from fabrics, and uniquely identified in the presence of other dyes that are used in the printing and dyeing of such materials, by LDMS. In these experiments, no extraction step is required. A pulsed UV laser directly irradiates a paper or fabric sample—colorants are desorbed, ionized and detected using time-of-flight MS. Results shown here suggest that dyes such as Basic Red 1:1 and Basic Violet 11:1 are used in such devices.

KEYWORDS: forensic science, laser desorption mass spectrometry, security inks, currency, fabric

A variety of degradation technologies are available to protect bank currency, ATM cash, safe contents or pavement transport from theft or unauthorized removal. The system can be classified under two general types; those using staining ink and those using smoke and dye. The ink systems are typically pressurized to release a concentrated spray of indelible red ink over the currency in ATM cassettes when activated by sensors in the machine. These inks, mixtures of staining dyes and a vehicle, are referred to here as security inks. The smoke and dye systems release a hot cloud of red smoke, red dye and optional tear gas to disrupt the criminal activity. The tear gas, containing compounds such as orthochlorobenzalmalonitrile and chloroacetophenone, is an effective lachrymator that can temporarily disrupt a robbery in progress. The dyes, when released from the various devices, mark both the money and the perpetrator, creating evidence. The detection and identification of security dyes on currency, and on items of clothing, can link a suspect to a robbery.

Some dye and lacrymator residues can be detected using gas chromatography/mass spectrometry. The use of GC/MS for such analyses, with a variety of ionization techniques, was evaluated by Martz, Reutter and Lasswell (1). Liquid chromatography/mass spectrometry has also been used to analyze similar systems, notably pepper spray residues on fabrics (2). Methods for washing security dyes from U.S. currency have been reported/evaluated as well (3).

It has recently been reported that laser desorption mass spectrometry (LDMS) can be used to analyze dyes directly from paper.

The focus of previous work has been on pen inks (4–6) and dyes of interest in the art world (7). In these experiments, a pulsed UV laser is focused directly on ink/dye samples, usually on paper. While all components of the ink and paper are irradiated, only the dye molecules absorb the UV radiation and are subsequently desorbed/ionized for mass spectrometric analysis.

Laser desorption is a rapid heating technique, in which absorbing molecules usually desorb intact. Molecules exhibit a clear “charge-state signature” in that, if the dye is cationic, only positive ions are formed; if the dye is anionic, only negative ions are formed. The signature of a neutral dye is the formation of both positive and negative ions (4–7).

Reported here is the use of LDMS for the identification of dyes, such as those used in North America and Europe to protect ATM cash, directly from currency and fabrics. These dye components can be detected at low levels, following attempts to remove them using soaps and solvents. Some of the colorants used to print the currency and fabrics can be detected as well. LDMS can be used to detect security dyes or fabric dyes on a single thread of fabric. These results will be presented here.

Experimental

Chemicals—Security ink (a staining ink) and stained bills were provided by 3SI Security Systems (Exton, PA). Solvents and cesium iodide were obtained from the Sigma-Aldrich Chemical Company (Milwaukee, WI). RIT color remover (Bestfoods Specialty Products, Indianapolis, IN), Gain laundry detergent (Proctor and Gamble, Cincinnati, OH), bleach (The Clorox Co., Oakland, CA), and nail polish remover (Wholesale Merchandisers, Grand Rapids, MI) were purchased locally.

Instrumentation—A PerSeptive Biosystems Voyager delayed extraction laser desorption time-of-flight mass spectrometer

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(PerSeptive Biosystems, Inc. Framingham, MA), outfitted with a pulsed nitrogen laser (3 ns, 337 nm, ThermoLaser Science, Franklin, MA) was used for each of the experiments. The accelerating voltage used was +20 keV, delayed-extraction times ranged from 50 to 150 ns, the guide wire ranged from 0.05% to 0.2% of the accelerating voltage (but with the opposite sign), and the grid voltage was 94.5% of the accelerating voltage. Cesium iodide was used as a calibration standard.

Sample Preparation—The security ink was blotted directly onto a piece of plain printer paper for neat analysis. For the analysis of the currency, a portion of the stained (or washed) bill was mounted to the sample plate and inserted directly into the instrument. For the analysis of the fabric, a portion of the stained (or washed) fabric was mounted directly to the sample plate and inserted into the instrument. “Disposable” MALDI plates that are available from the instrument manufacturer are preferred because the flat surface of these plates is recessed, preventing the sample from interfering with the ion source components. If one begins with a new sample, the total time to mount it on a sample plate, introduce it into the vacuum system of the mass spectrometer, and obtain positive and negative ion LDMS spectra, is 10 min or less.

Washing of Stained Currency—Strips of stained currency (approximately 1 cm × 2 cm) were immersed and intermittently sonicated in approximately 2 mL of solvent for up to 24 h. The solvents used were: dichloromethane, distilled water, isopropyl alcohol, cyclohexanone, benzene, nitric acid, tetrahydrofuran, acetone, ethanol, bleach, RIT color remover (approximately 50 mg RIT in 2 mL water), Gain laundry detergent (approximately 50 mg detergent in 2 mL water), and nonacetone nailpolish remover (ethyl acetate-based). Three sets of stained currency were used: bills stained over one year ago, bills stained in our laboratory one week prior to washing, and bills stained in our laboratory one hour prior to washing.

Washing of Stained Fabric—Samples of stained fabric (approximately 1 cm × 3 cm) were immersed and intermittently sonicated in approximately 20 mL of solvent over the course of one, two, and three days (with periodic solvent replenishment). The solvents used were: dichloromethane, distilled water, isopropyl alcohol, cyclo-

hexanone, benzene, nitric acid, tetrahydrofuran, acetone, ethanol, bleach, RIT color remover (approximately 0.25 g RIT in 20 mL water), Gain laundry detergent (approximately 0.25 g detergent in 20 mL water), and nonacetone nailpolish remover (ethyl acetate-based). Several natural and synthetic fabrics were used, all had been stained approximately 36 h prior to washing.

Thin Layer Chromatography—For TLC separation of the components of the security ink, the stock ink solution was diluted using acetone and spotted onto standard 5 cm × 10 cm silica gel TLC plates (Sigma-Aldrich). The mobile phase was 52% ethyl acetate, 26% ethanol and 22% water.

Results and Discussion

Detection on US Paper Currency

Currency stained red by security ink from an activated security device was obtained from a manufacturer. A red stained portion of a one dollar bill was analyzed by LDMS. When the pulsed UV laser radiation was focused onto the red stain, ions were formed and detected. A portion of the positive ion mass spectrum obtained is shown in Fig. 1A. Similar mass spectral results were obtained in the analysis of bills stained one year before analysis, one week before analysis, and immediately before analysis. There are two dominant peaks in the mass spectrum, at m/z 429 and 457, which represent two major red dye components. The compounds do not yield negative ions, indicating that they are both cationic dyes. The isotopic peaks are informative. For example, if the molecule contains only C,H,N and O, the peak at m/z 429 represents the molecule in its monoisotopic form. The peak at m/z 430 shows that a fraction of the molecules will exist in nature containing one ^{13}C . The isotopic peaks for m/z 429 and 457 both suggest that they are simple organic molecules. It is unlikely that they are metal-complexes, and it is clear that they do not contain Cl or Br, since the isotopic patterns are simple. To determine whether the peaks seen in Fig. 1A are actually due to the security ink, or if they are components of paper currency in general, a positive ion LDMS spectrum was obtained (over the m/z range of 1–3500) for a portion of a one dollar bill that was neither stained nor printed. In this spectrum (not

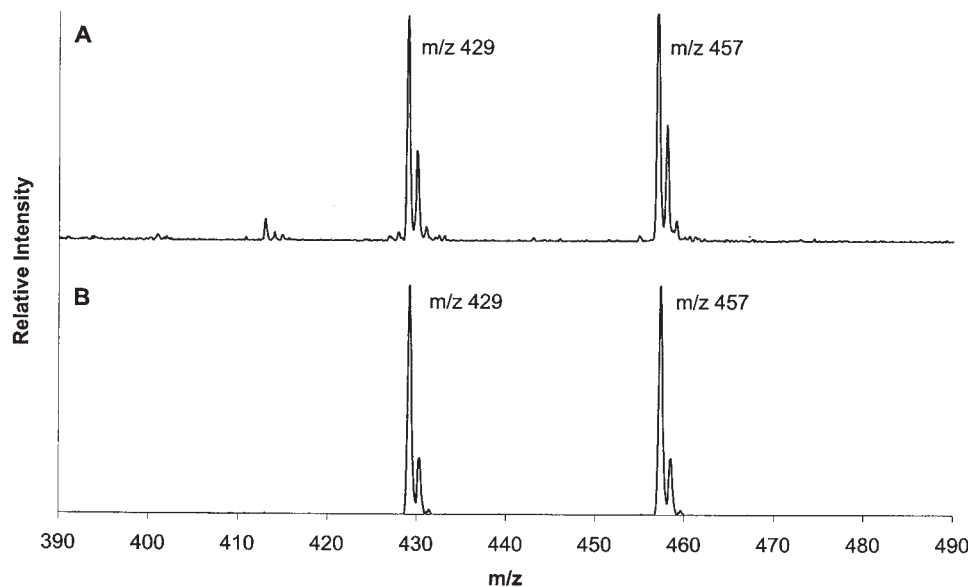


FIG. 1—Positive ion mass spectra of security ink-stained A) Currency, and B) Cotton fabric.

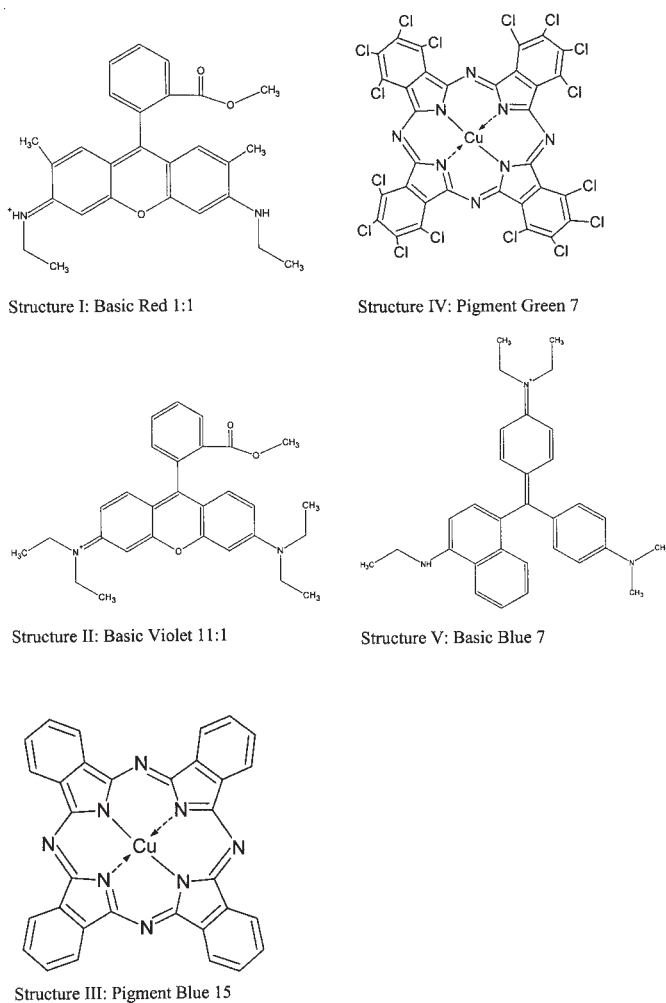


FIG. 2—Dye structures.

shown), there were no peaks, except for low m/z peaks at m/z 23 and 39 representing Na^+ and K^+ . These are always present in such samples.

A search of the literature for organic dyes that are cationic, red, and have molecular weights of 429 and 457 yielded the tentative assignments Basic Red 1:1, (Structure I in Fig. 2), and Basic Violet 11:1 (Structure II). The molecular formula of each is consistent with the isotopic peaks detected. These are two rhodamine dyes, and are likely candidates for use in such an application.

When the sample was moved such that the laser irradiated printed portions of the dollar bill, dyes used to print the bill could be detected. US paper currency is printed using an intaglio process, and the ink contains a number of components. We do not suggest here that they can all be detected, rather that some dye components will desorb and ionize when subjected to pulsed UV radiation. When the laser illuminates the black printing ink on the dollar bill, a major peak in the resulting mass spectrum results, at m/z 575. This peak and its isotopic variants are shown in Fig. 3. Clearly, the isotopic pattern is much different than the simple "descending pattern" observed in Fig. 1A. The alternating peak intensities suggest the presence of one or more elements that have abundant isotopic forms two mass units above their most abundant form. Chlorine is one example, having two isotopic forms, ^{35}Cl (76%) and ^{37}Cl (24%). Another example is copper, consisting of ^{63}Cu (69%) and ^{65}Cu (31%). The peaks at m/z 575 are assigned as representing Pigment Blue 15, copper phthalocyanine (Structure III). The insert in Fig. 3 shows the expected (theoretical) isotopic distribution for this compound, with the formula $\text{C}_{32}\text{H}_{16}\text{N}_8\text{Cu}$. In addition to the isotopic information provided, the compound yielded both positive and negative ions, indicating that the parent compound is neutral. In the 1998 US Patent 5,723,514 (Nachfolgen *et al.*, Sun Chemical Corporation) on heatset intaglio printing ink (8), several copper phthalocyanines are specifically listed as appropriate dye components, as are inorganic pigments such as iron oxides. Thus, the mass spectral information, relevant literature, and our prior experi-

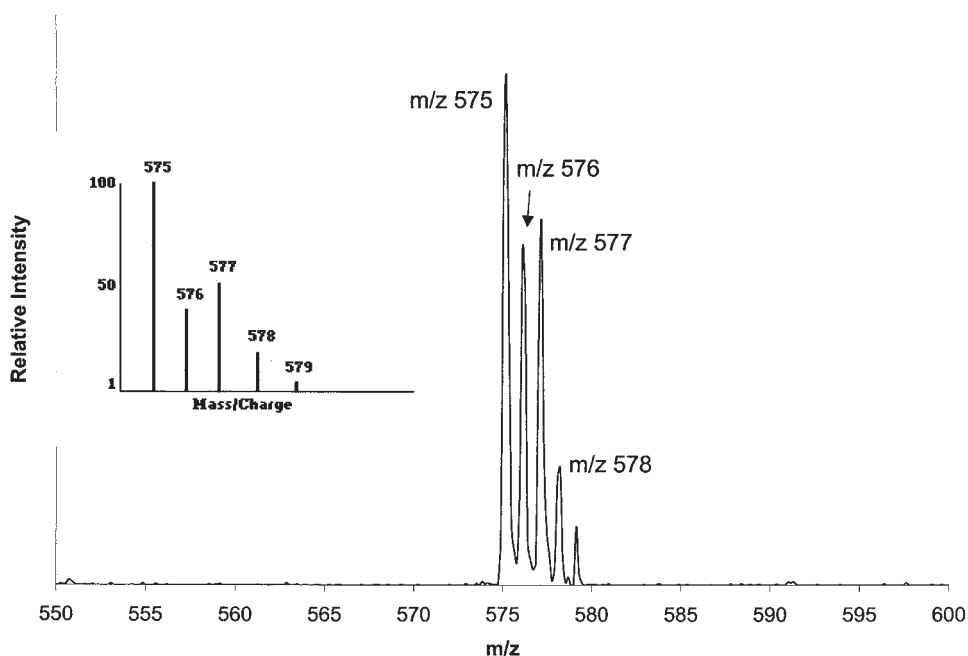


FIG. 3—Portion of the positive ion LDMS spectrum obtained from the black ink of US paper currency. The insert shows the theoretical isotopic distribution for a compound with the formula $\text{C}_{32}\text{H}_{16}\text{N}_8\text{Cu}$.

ence in the detection of copper phthalocyanine in a number of other colorants (7)—all of these support this assignment.

The irradiating laser was also focused on the green-printed portion of the dollar bill. For this ink region, copper phthalocyanine is again detected at m/z 575. In addition, there are higher mass peaks, above m/z 1000, in the positive ion LDMS mass spectrum. These are formed as both anions and cations, so they represent neutral dye molecules. A portion of the positive ion mass spectrum for the green currency ink is shown in Fig. 4. The isotopic patterns are complex, and at these higher m/z values, the mass spectral peaks are not completely resolved. The alternation of peak intensities separated by 2 Daltons suggests the presence of Cl. The complexity suggests the presence of multiple Cl atoms. Clusters of peaks, separated by the mass of Cl, reinforce the possibility. The major set of peaks around m/z 1126 are assigned to represent Pigment Green 7 (PG7, Structure IV). This represents copper phthalocyanine in which all 16 hydrogen atoms have been replaced by chlorine atoms. There are many such variations of copper phthalocyanine; substitutions on the outer rings can change solubility properties as well as allow for the color to be adjusted (9), in this case, from blue to green. The theoretical isotope distribution for Pigment Green 7 is shown as the insert in Fig. 4. Mass spectrometry can provide unique insights into molecular structure. While a manufacturer would report the molecular weight of Pigment Green 7 as 1126, there are actually many isotopic variants of the molecule that naturally exist, with molecular masses as low as 1118 and as high as 1137, depending on how many heavy atoms of each element are present.

The other peak clusters in Fig. 4 deserve comment. If the conversion of copper phthalocyanine to Cl_{16} -copper phthalocyanine is not complete, partially chlorinated forms will be present and will be detected. Two are shown here—representing Cl_{15} - and Cl_{14} -copper phthalocyanine, at m/z values 1092 and 1058. These are not “fragment ions” but additional components, likely impurities in the Pigment Green 7. The mass differences and unique isotopic clus-

ters support these assignments. There is also a cluster of peaks 23 Daltons higher than the molecular ion peak for Pigment Green 7. This is a sodium adduct, $(PG7 + Na^+)$. These are commonly seen for neutral dye molecules when salts are present.

Thus, while it was not anticipated, it is clear that LDMS can be used to detect some of the pigments used to print US currency. No evidence for other anticipated components such as iron oxides was found in the mass spectral data. Since spectra can be obtained quickly, the method potentially has application in the detection of counterfeit bills. Also, it is important to know what printing colorants are present and detectable, to determine if they might interfere with detection of the security ink dyes. They do not. In fact, they are easy to distinguish because lower laser powers are required to desorb security ink from currency than to desorb currency colorants. Thus, even if the only choice is to analyze a potential security ink spot that is on top of a printed portion of a bill, a low laser power can be used such that signals can be generated for the security ink dyes with no ions formed from the printing ink.

While Fig. 1A indicated the presence of two dyes used in the security ink, TLC analysis of the dye mixture indicated the presence of at least a third component—a blue dye. Two red bands appeared very close to the blue band, so when the blue dye was eluted off the TLC plate, some of the two red dyes were present as well. Nonetheless, a solution substantially enriched in the blue dye was generated and analyzed by LDMS from a standard gold LDMS sample plate (Fig. 5). The new peak, m/z 477, represents this blue dye. Isotopic peaks for m/z 477 are similar to those for the other peaks in Fig. 5, indicating that it probably contains only C, H, N and possibly O. No corresponding peak was observed in the negative ion spectrum, so the dye is blue, cationic, and has a molecular mass of 477 Daltons. One attractive possibility is Basic Blue 7 (structure V). The theoretical isotopic pattern for this ionic dye, $C_{33}H_{39}N_3^+$, is shown in the insert for Fig. 5. Thus, with some chromatographic assistance, a third dye can be found in the security ink. While LDMS can detect subnanomolar amounts of analyte, the

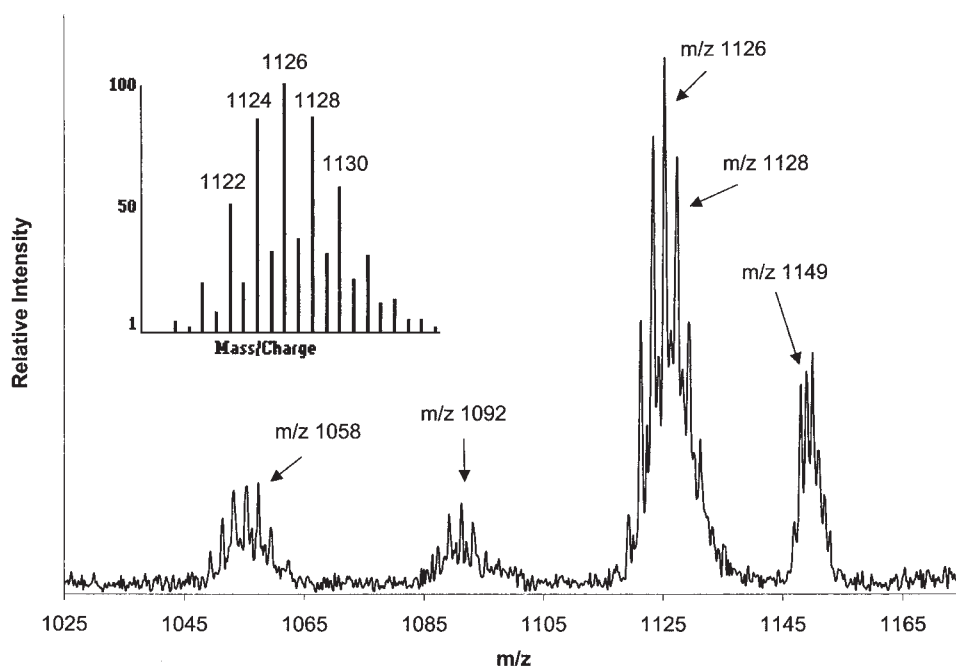


FIG. 4—Portion of the positive ion LDMS spectrum obtained from the green ink of US paper currency. The theoretical isotope distribution for Pigment Green 7 is shown in the insert.

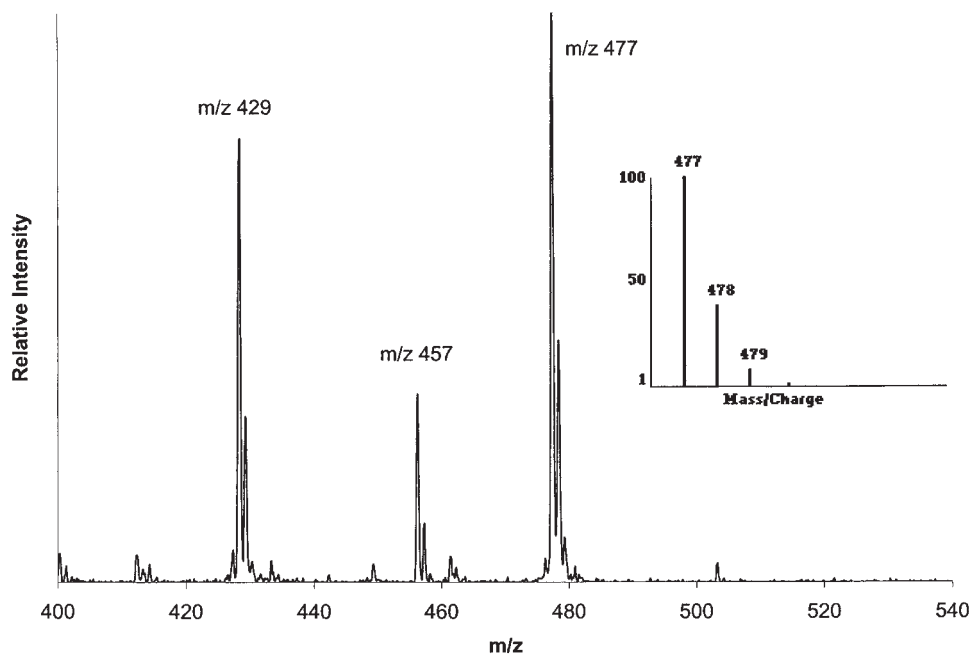


FIG. 5—Positive ion LDMS spectrum of security ink dyes, following TLC separation, yielding predominantly a blue dye. The insert shows the theoretical isotopic distribution for Basic Blue 7.

limited dynamic range of the technique hinders the simultaneous detection of a minor component (such as Basic Blue 7) in the presence of a major component (such as the red rhodamines) of the sample.

It is our experience that, even at very low levels where the red rhodamine dyes cannot be clearly detected by visual inspection, the LDMS experiment can detect both dyes, as in Fig. 1A. To simulate what may be done with security-ink stained money (3), in an effort to wash the stain off, we exposed stained portions of paper currency to dichloromethane, water, isopropanol, cyclohexanone, benzene, tetrahydrofuran, acetone, ethanol, bleach, nitric acid, laundry detergents, the commercial product RIT Stain Remover, and ethyl acetate-based fingernail polish remover. All removed a substantial amount of the dyes, leaving only a faint pink color behind. In strong acids such as nitric acid, treatment for an hour or more resulted in noticeable damage to the paper. In all cases, after dye extraction and washing of the sample, the two dyes could be easily detected by LDMS.

With this experience in analyzing red security-ink stained currency, we began to notice a number of bills in circulation that have red ink on them. The stains are most often in one corner of the bill. LDMS does yield spectra of these red inks, and in no case has the spectrum matched that of the security ink studied here. The marked bills found in circulation were all ten and twenty dollar bills. An inquiry at a local bank led to facts on the surprising practice that some banks mark packs of money that are put into ATMs, to assist optical devices inside the machine in detecting the presence/movement of individual bills. The marks are added by bank staff using standard, wide-tip felt markers (frequently red or black). Thus, the presence of a red ink mark on a twenty dollar bill does not necessarily indicate that it had been involved in a robbery, more likely that it has passed through an ATM.

If an ATM has been tampered with and a security device is triggered, the results may include not only dye-stained currency, but dye-stained clothing. This certainly involves a much more complex

matrix from which one may be asked to detect staining dyes. For example, on a multicolored shirt such as a flannel shirt, it would be challenging to visually determine the presence of a security dye, even when present in a substantial amount, if the colors in the shirt were similar. Therefore, it was useful to demonstrate that LDMS could be used for the direct analysis of security ink dyes from fabrics, without having to extract or perform any chemical manipulation.

Detection on Cotton Fabric

A white cotton fabric on which a pattern involving yellow, teal, chartreuse, black and salmon-colored figures was printed, was selected for study. As in the case of unprinted portions of paper currency, white fabric does not yield a significant LDMS mass spectrum. If the laser power is increased, small peaks such as those shown in Fig. 6 are detected, at low signal-to-noise ratios. If the laser is moved to irradiate a yellow portion of the fabric, a portion of the resulting spectrum is shown in Fig. 7A. It is unclear at this time what dyes are represented by these peaks. The mass spectral resolution suffers from the experimental design. Conducting a MS experiment based on a time-of-flight measurement, using an insulating material such as cotton, is less than ideal. Of interest is the cluster of isotopic peaks around m/z 250, and a second set around m/z 275. The spacing of the isotopic peaks suggests the presence of chlorine. While no positive assignment will be made here, we did recall a similar spectrum that had been obtained in a very different experiment, which is shown as Fig. 7B. The isotopic peaks appear to be the same, as well as the relative abundances of the two components that yield the peaks at m/z 250 and 275. The spectrum in Fig. 7B was obtained from the yellow ink used to print a postage stamp, and appears to be the same as the compound(s) used to print the fabric. The stamp, a 37 cent US teddy bear stamp (issued 8/15/02) was printed using 4 color offset printing. In the margin of a sheet of these stamps, samples of each ink used in the printing are available. Figure 8 shows a

portion of the positive ion LDMS spectrum of the chartreuse (yellow-green)—colored portion of the cotton fabric. In this case, the m/z 575 peaks represent copper phthalocyanine, the m/z 1050 and 1125 peaks represent chlorinated copper phthalocyanine, and the “yellow peaks” at m/z 250 and 275 are still present. This example shows the extent to which similar dyes are used in a variety of printing methods, such as those used for printing stamps, and creating color patterns on inexpensive material. It also shows the wide variety of uses for copper phthalocyanines. The fact that the spectra from fabric exhibit lower resolution may be reflective of the rough

nature of the surface, leading to a range of flight times for ions formed at different locations on that surface.

When security inks are present on fabric, they can be detected at low laser powers, yielding spectra such as Fig. 1B. They can be desorbed and ionized at laser powers lower than those capable of desorbing some fabric colorants, making the LDMS method for detection of security inks unique. If a scientist was attempting to determine the presence of a security ink on a red and purple plaid shirt, it would probably be a straight-forward analysis, since many fabric dyes cannot be desorbed. In many instances, fabrics are dyed

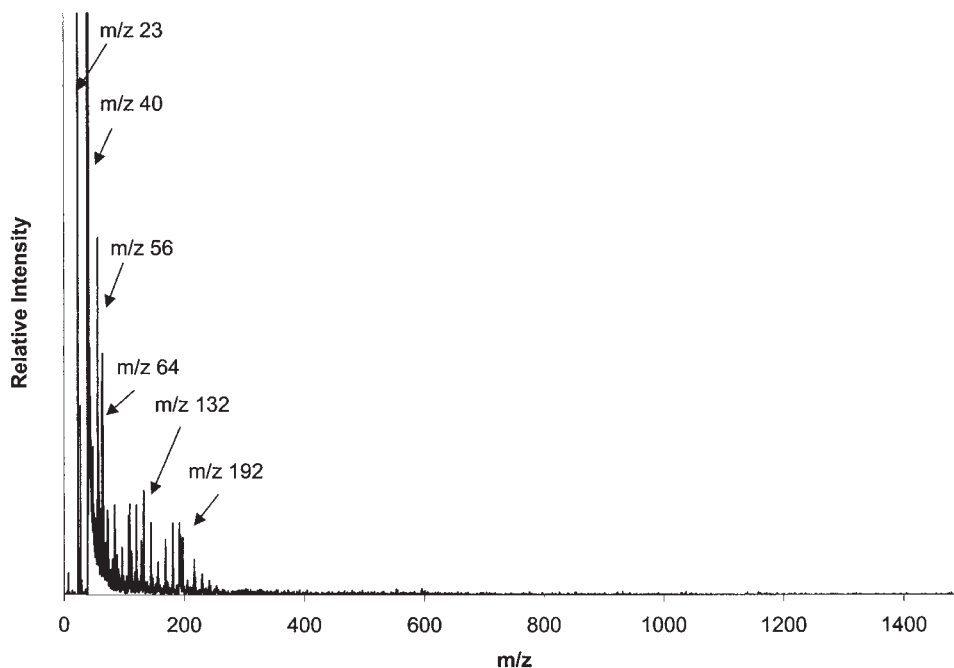


FIG. 6—Positive ion LDMS spectrum of white cotton fabric.

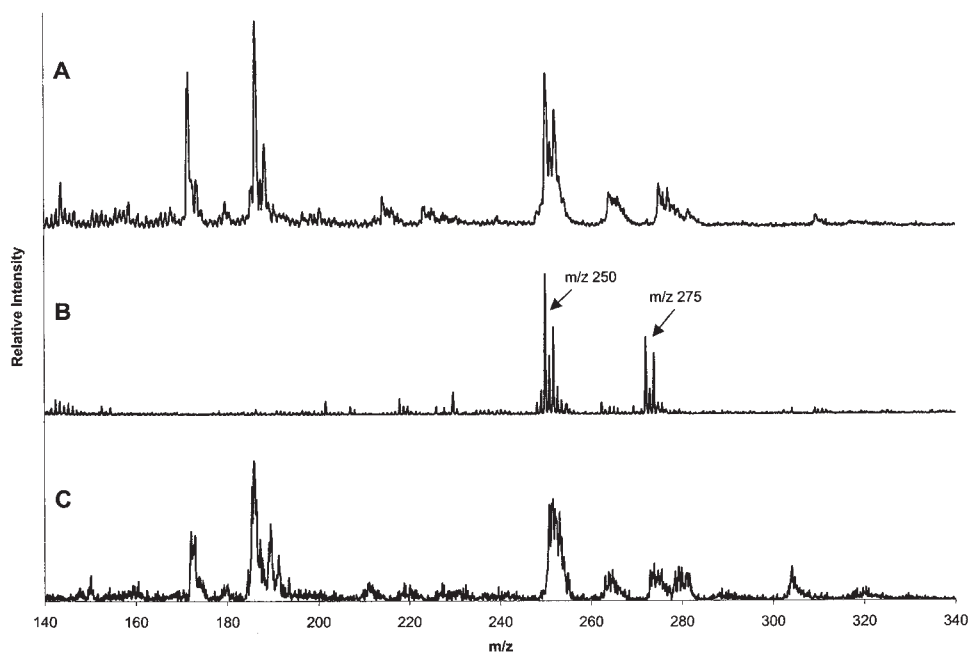


FIG. 7—A) Positive ion LDMS spectrum of yellow dye used to dye white cotton fabric. B) Positive ion LDMS spectrum of a yellow dye used in the printing of a postage stamp. C) Positive ion LDMS spectrum of a single cotton fiber containing the same yellow dye.

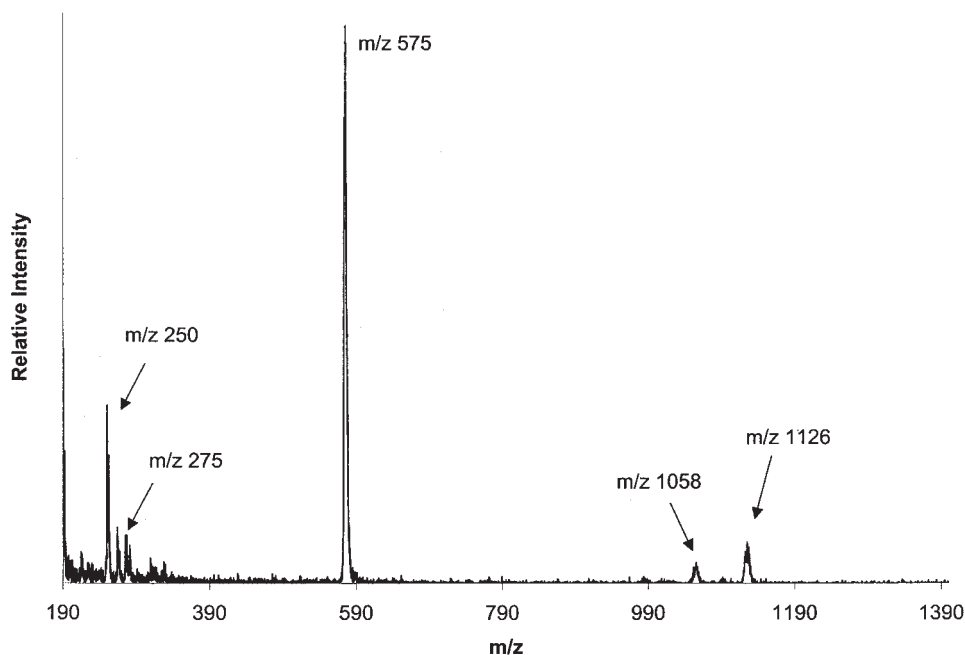


FIG. 8—Positive ion LDMS spectrum of a teal color printed on a white cotton fabric.

by polyanionic, covalently-bound (“reactive”) dye molecules (10)—in such cases, since LDMS does not break covalent bonds, no gas phase dye ions are detected. Thus, many fabric dyes may well absorb UV laser irradiation, but the laser power deposited may be insufficient to break covalent bonds.

The spectrum in Fig. 7C bears obvious similarities to 7A, except that the resolution and signal-to-noise ratio is poorer. The spectrum in Fig. 7C was obtained from a single yellow fiber of cotton fabric, from the fabric studied here. The laser spot can only be focused to a diameter of several fiber widths, so much more sample is irradiated when the laser is focused on a solid fabric than a single fiber. However, we have shown that desorbable fabric dyes, as well as security inks, can be easily detected from single fibers. This is obviously important, since single fibers represent an important class of trace evidence.

Conclusions

It is demonstrated here that LDMS is an effective analytical tool in the detection and identification of security ink on surfaces such as paper and fabric. The data obtained for the two main dye components of this security ink are consistent with the structures for Basic Red 1:1 and Basic Violet 11:1. Whatever the actual structures, they are clearly not the most commonly used red rhodamine dyes such as those found in red pens, Basic Red 1 (Rhodamine 6G) or Basic Violet 10 (Basic Red B), since these isomers each yield a mass spectral peak with an m/z value of 443, not m/z 429 and m/z 457 as observed. Thus, while the particular dyes were clearly chosen for specific reactive and spectroscopic characteristics, they are also unique on the basis of their molecular mass. LDMS is able to distinguish between compounds of the same chemical class (which may yield indistinguishable UV and IR spectra) as long as the compounds vary in mass.

The direct detection of intaglio printing inks used to print currency and the direct detection of dyes used in coloring fabric are both of obvious forensic interest. The spectra presented here further demonstrate the versatility of LDMS.

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