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PAPER

QUESTIONED DOCUMENTS; CRIMINALISTICS

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Analysis of Pigmented Inkjet Printer Inks and Printed Documents by Laser Desorption/Mass Spectrometry*,†

ABSTRACT: Anyone with a computer, scanner, and color printer has the capability for creating documents such as identification cards, passports, and counterfeit currency. Laser desorption mass spectrometry (LDMS) has been demonstrated as a powerful tool for colorant analysis. Inkjet printers are now moving largely toward the use of pigments as colorants; their insolubility makes analysis by simpler methods such as thin-layer chromatography no longer an option. Recent developments in pigmented inkjet printer inks, such as gloss optimizers that coat pigment particles, may prohibit colorant analysis by LDMS. We demonstrate here that pigments used in inks from two Epson printers can be detected and analyzed by LDMS. Also, LDMS spectra of various colors created using a 4-cartridge (cyan/magenta/yellow/black, CMYK) inkset are evaluated, to begin to develop an approach for unraveling LDMS data from real samples, to determine the number of inks used by a printer, and the chemical composition of the colorants.

KEYWORDS: forensic science, questioned document examination, pigments, inkjet printing, mass spectrometry, inks

Laser desorption mass spectrometry (LDMS) has been developed as a tool for questioned document analysis, with a focus on the analysis of colorants (1). This work began in 2001, with the analysis of ballpoint pen ink dyes (2–5), and has been extended to the analysis colorants used in art (6,7), and pigments, including those used in pigmented pen inks (8). The advantages of LDMS include the ability to perform analyses of colorants directly on substrates, without the need for an extraction step, and sensitivity for some compounds that approach the picomole level. For analysis of ink on paper, most of the components of the ink and paper do not absorb light at 337 nm, the wavelength of the laser light used, while most colorants do. Thus, the method allows for the selective detection and analysis of dye and pigment colorants. The focus of this work is on the analysis of pigmented inkjet printer inks.

Inkjet printers became commercially available in the 1970's, marketed initially as low-resolution printers for high speed printing of labels and cardboard boxes (9). Now the most popular type of desktop printer, inkjet-printing technology continues to improve for increased performance, especially regarding increased resolution. When low-cost digital cameras appeared on the market, one limitation for their use was the generation of prints. Photos printed on inkjet printers would quickly fade (10), since these printers initially used inks containing dyes as colorants, which were not lightfast. Now, inkjet printers that use pigment-based inks are available. These inks can generate "archival quality" prints, that remain stable for more than 100 years (11,12). While the introduction of pigments in inkjet ink can provide superior prints, it created a challenge for document examiners, who traditionally analyzed colorants using thin layer chromatography (TLC). While TLC is an appropriate tool for analyzing soluble dyes, pigments are insoluble particles, thus TLC cannot be used.

In the LDMS analysis of colorants in a pen stroke on paper (1), light from a pulsed UV laser is focused onto the sample in the ion source of a time-of-flight mass spectrometer. Molecules that absorb the 337 nm photons from the nitrogen laser can be desorbed and ionized, with the resulting gas phase ions, both positive and negative, subsequently analyzed. The situation is different when the sample is not a continuous pen stroke, but generated by an inkjet printer. Inkjet printed documents do not provide a continuous region of color. Droplets, that may be on the order of a picoliter or less, are deposited onto the substrate. Depending on the printer resolution and the paper used, either isolated spots or overlapping spots of color may compose the target for analysis, presenting a unique analytical challenge. Pigmented inks can be much more chemically complex than dye-based inks. Pigment particles have the tendency to settle in an ink cartridge (as pigments settle in a can of house paint), unless compounds are added to maintain a suspension of the particles in the ink. Inks may contain buffers, humectants, chelating agents for metals, biocides, UV-blockers, and surfactants (9). Some of these components serve to control the spread of the droplet and improve drying time. Two aspects of inkjet printing are of particular concern when LDMS is the method of analysis: (i) manufacturers discuss the encapsulation of each pigment particle in an acrylic resin (13); (ii) other manufacturers use a clear gloss optimizer to coat the entire surface after the ink has been applied (14). Either could prohibit the formation of gas phase ions from laser irradiation of the pigments, because ions formed on the pigment surface could not penetrate the clear coating. Users rarely appreciate how chemically complex their printer may be. For example, in 1997, Canon introduced a method called Plain Paper Optimized Printing, P-POP (15). To reduce spreading of ink on plain paper, they used an ink optimizer. This was contained in a

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reservoir that was concealed within the black ink cartridge. The printer would deposit a dot of ink optimizer liquid before an ink dot was deposited, at the same location. The optimizer "sets" the dyes, so they do not spread. It is unclear what, chemically, "setting" means, and whether it results in a chemical modification. Thus, a number of chemical approaches have been used to stabilize very small dots of color, on a surface, that could prohibit analysis by LDMS.

The long-term goal of this project is to develop LDMS for the analysis of inkjet-printed documents such as forgeries or counterfeit currency. From the analysis, the number of pigments used by the printer, and the chemical identity of each would be determined. This information could be used to identify the class of printer, or perhaps a specific printer, as part of the questioned document analysis. For example, the information could be used to determine if the printer was an inexpensive one, using a CMYK (cyan/magenta/yellow/black) ink system, or from a higher priced printer which uses a larger number of ink cartridges.

To achieve this goal, the first challenge is to determine whether pigments used in pigmented inkjet printer inks can be analyzed using LDMS. If this is possible, the second goal is to develop an approach for determining the number and identity of inks used to print a color document.

Materials and Methods

The PE Biosystems Voyager DE time-of-flight mass spectrometer (Framingham, MA) is equipped with a pulsed nitrogen laser (337 nm) and a linear time-of-flight mass spectrometer. For the analysis of positive (negative) ions formed by LD, a sample plate on which the analytes are placed is held at +20,000 V (−18,000 V), an intermediate acceleration grid in the ion source is held at 94.5% of the accelerating voltage, and a delay time of 100 ns is used between the laser irradiation pulse and initiation of ion acceleration. In a typical experiment, ink on paper from an Epson C80 or C88+ inkjet printer (Epson America, Inc., Long Beach, CA) is secured onto a modified sample introduction plate using double-stick tape (3M Scotch Brand, St. Paul, MN). All samples were printed on Boise Aspen 30 white paper (Boise, ID). While the inks used in these printers are pigmented inks, an attempt was made to analyze each by TLC. The solvent system used was 70:35:30 (v:v:v) ethyl acetate:ethanol:water. The TLC plates used were Whatman Partisil K6 (Piscataway, NJ) (60 Angstrom silica gel, 250 μm layer thickness). The same solvent was also used with a yellow ink, on Whatman paper, to separate an apparent dye from the yellow pigment, for subsequent LDMS analysis.

Results and Discussion

Positive and negative ion LDMS spectra of inks from two similar Epson printers are presented and discussed here. Both the Epson Stylus C80 and C88+ are CMYK printers. The C80 was introduced in 2001 and the C88 series in 2005. Both use pigmented inks (Epson DuraBrite [Epson America, Inc.] in the C80 and DuraBrite Ultra [Epson America, Inc.] in the C88+). The newer C88+ has twice the (maximum) printing resolution, 5760 × 1440 dpi, as the older model, and produces ink droplets as small as 3 pL.

For this initial study, to determine whether LDMS can be used to analyze pigmented inkjet printer inks, samples from these two printers were created both from printed documents, and by extracting ink from the four cartridges and manually applying it to paper. If a printer has a yellow ink, for example, it is not trivial to have it print pure yellow ink on paper. If one uses any simple program, draws and prints a yellow box, that yellow may not correspond to the exact color of the yellow ink, so the printed yellow box will contain other inks. To get printed samples of the pure inks on paper, diagnostic, or alignment sheets that contain blocks or lines of each ink were used. For some colors, both printers use the same pigments.

Black Pigmented Inks

The positive and negative ion LDMS spectra of the black pigmented ink on paper from the C88+ printer are shown in Fig. 1. The same results were obtained for the black ink from the C80 printer. The positive and negative spectra are very different, and are typical for black inks based on the pigment carbon black. Figure 1*a* contains no information about the pigment, but shows a series of high *m/z* peaks separated by 44 Daltons (Da), typical for a set of polyethylene glycol (PEG) oligomers. There are actually two overlapping sets of peaks separated by 44 Da, one beginning at *m/z* 425 and the other, more intense set of peaks, beginning at 441. These two series differ by 16 Da, the difference in mass between Na^+ and K^+. Thus, two series of PEG complexes are observed—one where each member is attached to a sodium ion, the other, potassium ions. The fact that the K^+-adduct ions are more abundant than the Na^+-adducts correlates with the fact that more K^+ ions are present in the sample, as can be seen by the low mass peaks at *m/z* 23 and 39.

While a series of peaks separated by 44 Da could easily be labeled as representing polyethylene glycols, if one chooses to define their specific composition, it becomes a challenge.

If the *m/z* values are analyzed under the assumption that they represent alkali ion adducts of H-$(C_2H_4O)_n$-OH, the masses do not correspond to integer values of *n*, so they are not, in fact, PEG oligomer adduct ions, but instead represent a set of molecules that contain different numbers of C_2H_4O units. One interesting possibility is the surfactants sold by Air Products under the family name of Surfynol, with the general structure

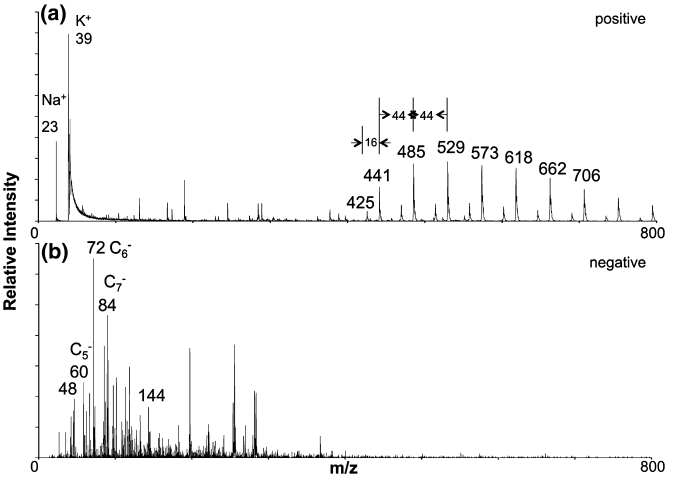

FIG. 1—*(a) Positive and (b) negative ion LDMS spectra of a black pigmented inkjet ink. The positive ion spectrum shows the presence of an oligomeric mixture, and the negative ions show the presence of the carbon black pigment, through a series of peaks representing* C_n^- *ions.*

$$HO-(CH_2CH_2O)_m-C(CH_3)(i-C_4H_9)-C \\ =C-C(CH_3)(i-C_4H_9)-(CH_2CH_2O)_n-OH.$$

For example, the mass spectral peak at *m/z* 441 is believed to be a K^+ adduct of a neutral molecule. The molecule would have a mass of 402. This could be a surfynol with $m + n = 4$. The oligomers could have $m + n > 4$; for example, the peak at *m/z* 706 would correspond to a K^+ adduct of a surfynol with $m + n = 10$. Thus, we believe that the collection of peaks represent a surfactant, often identified in inkjet printer material safety data sheets as "poly(oxy-1,2-ethanediyl), α,α'-[1,4-dimethyl-1,4-bis-(2-methylpropyl)-2-butyne-1,4-diyl]bis[ω-hydroxy-." The wetting and adsorption characteristics of these acetylenic diol-based nonionic surfactants on pigments such as carbon black and copper phthalocyanine have been studied by Musselman and Chandler (16).

Surfynol adduct ions are observed containing a range of C_2H_4O units, from $m + n = 4$ (*m/z* 441) to 15 (*m/z* 926). The average is 9, so the surfactant contained in the ink may correspond to Surfynol 440, defined as containing 10 ethylene oxide units. It is probably not Surfynol 104, which contains an average of 3.5 ethylene oxides, or Surfynol 465, for which the average is 20. If a weighted average is computed from the spectrum, considering the relative intensities of each of the peaks, we estimate that the collected mixture corresponds to an average of 7.6 ethylene oxide monomer units per molecule. Thus, we propose that the peaks in the positive ion spectrum, Fig. 1*a*, represent not PEG, but a surfactant which is known to be used in inkjet printer inks (17). Also, since adduct ions are generated, the molecule itself is uncharged. Alkali ions usually assist in the detection of compounds that do not contain an easily ionizable atom such as nitrogen, but do have oxygen-containing polar groups. Also, a portion of the added surfactant resides on the surface of the pigment particles, where laser energy is absorbed, so it is not unreasonable that such molecules have an opportunity to undergo desorption/ionization, even though they do not directly absorb the laser light.

In Fig. 1*b*, the negative ion spectrum, there is a set of peaks separated by 12 Da, *m/z* 48, 60, 72, 84, etc., which represent C_n^- anions. These are commonly seen when carbon black is the pigment, such as in the analysis of a black pigmented pen ink by LDMS (8).

Cyan Pigmented Inks

Figure 2*a,b* shows the positive and negative ion LDMS spectra of the cyan pigmented ink on paper, from the Epson C80 printer. The intense peak in Fig. 2*a* at *m/z* 575, with the isotope distribution as shown, indicates the presence of copper phthalocyanine, which is almost exclusively used as the cyan pigment in pigmented inks (18). The positive ion spectrum for the C88+ cyan ink is identical. The structure and formula are shown as an inset in Fig. 2*b*. The unique isotope pattern is in part because of the fact that copper has two abundant isotopes, ^{63}Cu and ^{65}Cu. In the LDMS experiment, the molecule is ionized by loss/gain of an electron to form, in separate processes, both M^+ and M^-. In Fig. 2*b* there is a small peak at *m/z* 654, which is 79 Da higher in mass than the molecular anion. There is no corresponding peak in the positive ion spectrum because *m/z* 654 represents the monosulfonated form of the pigment, which carries a negative charge. Pigment particles can be partially modified, by the replacement of H atoms with groups such as sulfonate groups, to increase particle stability or to form a dispersion (mixture of a pigment and a soluble dye) (19). Figure 2*c* shows the negative ion spectrum of the cyan pigmented ink from the C88+ printer. Clearly, the amount of the sulfonated copper phthalocyanine is increased, as indicated by the intense peak at *m/z* 654. This demonstrates the importance of collecting both positive and negative LDMS spectra. While the two cyan inks cannot be distinguished in the positive ion mode, the modified copper phthalocyanine, containing an anionic group, can only be observed in negative ion mode, allowing for a distinction to be made between the two cyan inks.

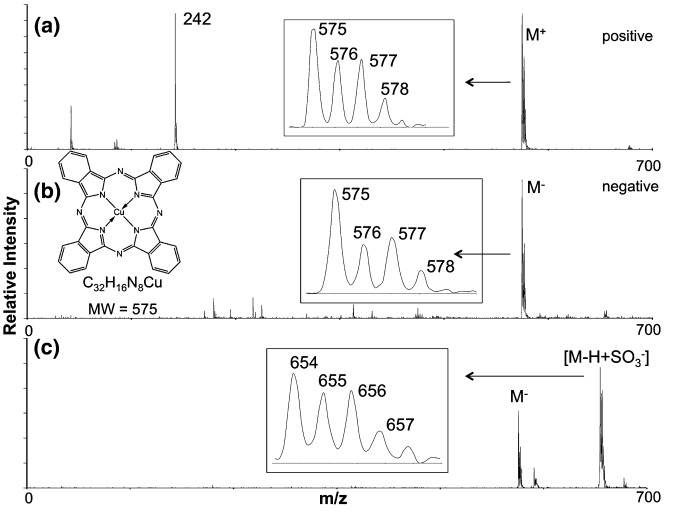

FIG. 2—*(a) Positive and (b) negative ion LDMS spectra of a cyan pigmented ink on paper from the Epson C80 Printer. (c) The negative ion LDMS spectrum for the cyan pigmented ink from the newer C88+ inkjet printer.*

Magenta Pigmented Inks

Figure 3 shows the positive and negative ion spectra for the magenta pigmented ink from the C88+ printer. In the positive ion spectrum, apart from the low mass sodium and potassium ion peaks, there is a cluster of peaks around *m/z* 313. As there is a peak at *m/z* 312, this suggests that there are two overlapping

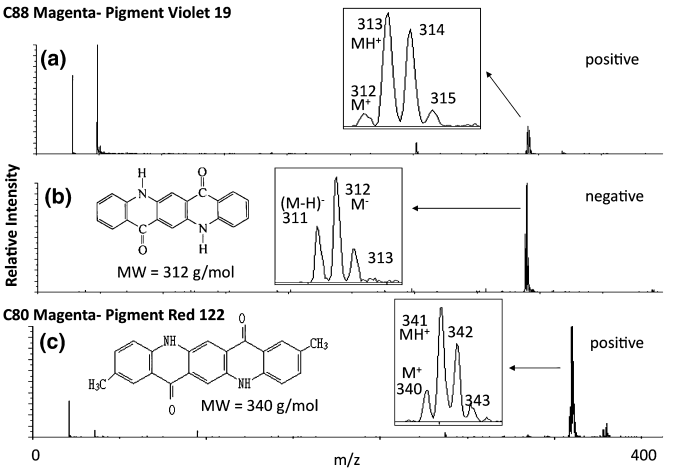

FIG. 3—*(a) Positive and (b) negative ion LDMS spectra of a magenta pigmented ink on paper from the Epson C88+ inkjet printer. The color, types of molecular ions formed, and isotopic pattern, is consistent with the pigment shown, Pigment Violet 19. (c) The positive ion LDMS spectrum of the magenta pigmented ink on paper from the Epson C80 printer, 28 Da higher in mass, representing another commonly used pigment, Pigment Red 122. The* m/z *values of the peaks shift by 28 mass units [comparing (a) with (c)] because of the addition of two methyl groups.*

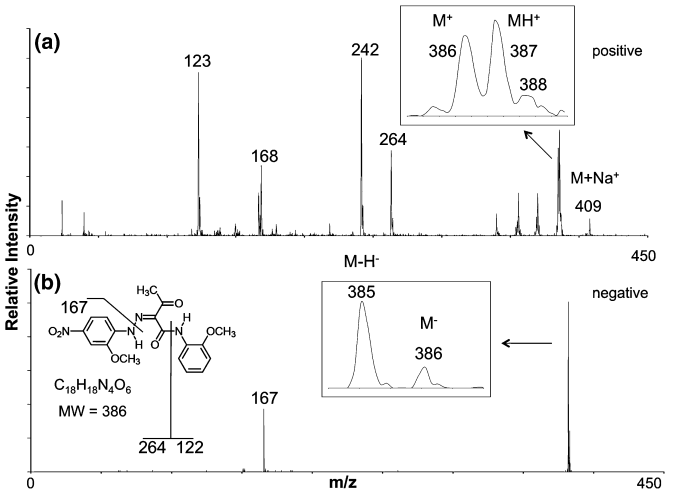

FIG. 4—*(a) Positive and (b) negative ion LDMS spectra of a yellow pigmented ink on paper from the Epson C88+ printer. The structure is shown for Pigment Yellow 74, a popular benzimidazolone pigment.*

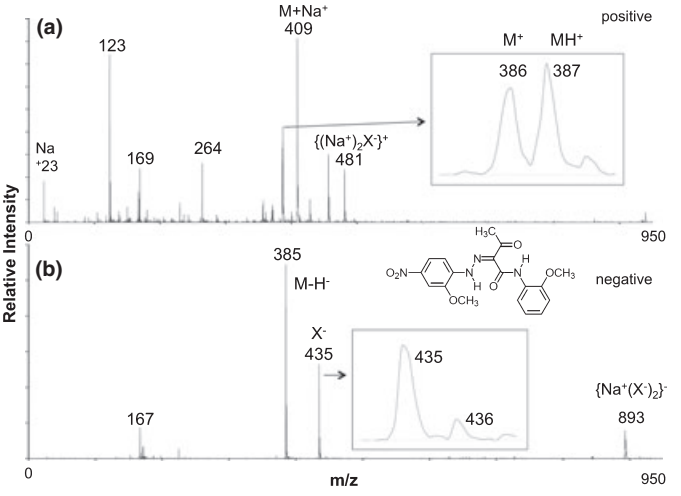

FIG. 5—*(a) Positive and (b) negative ion LDMS spectra of a yellow pigmented ink on paper from the Epson C80 printer. The spectra show the presence of the same yellow pigment as in Fig. 4, Pigment Yellow 74, and an additional anionic component.*

isotope distributions—two ions formed that differ in mass by 1, a molecular ion at *m/z* 312, and a protonated molecule at *m/z* 313. There is a peak at *m/z* 335, 22 Da above 313, a sodium ion adduct of the molecule with a MW of 312. The negative ion spectrum confirms the MW assignment, with the molecule forming both an intact molecular anion at *m/z* 312, and a deprotonated molecule at *m/z* 311. Isotopes do not suggest the presence of any heteroatom with a unique isotope distribution (Cu, Cl, Br, etc.). The various "molecular ions" that are formed are similar to what has been observed previously for fused ring quinacridone pigments (20). The molecular mass and the color are consistent with the structure shown, a common pigment known as Pigment Violet 19. The spectra look very similar for the magenta ink from the older C80 printer, although the peaks are shifted to higher mass by 28 Da (see Fig. 3*c*). We have previously encountered (20) Pigment Red 122, which has a MW of 340. It has the same structure as Pigment Violet 19 (shown in Fig. 3), with two H atoms replaced by CH_3– groups, shifting the mass by 28. Thus, the two printers use different magenta pigments, both quinacridones.

Yellow Pigmented Inks

Figure 4 shows the positive and negative ion LDMS spectra of the yellow pigmented ink from the C88+ printer. The peaks at *m/z* 386, 387, and 409 in the positive ion spectrum, and those at *m/z* 385 and 386 in the negative ion spectrum are consistent with a pigment MW of 386. Unlike the previous spectra in Fig. 3, there are additional intense peaks, some of which probably represent fragment ions. Fragment ions are most likely formed when the light-absorbing compound contains single skeletal bonds, such as in benzimidazolones. Fragment ions formed by cleavage of azo (N-N) and amide C(O)-N bonds have been observed previously (8,20); bond cleavage may be accompanied by a H-shift, either to or from the ionic fragment. A compound of this type, consistent with the MW, the color, and the fragment ions observed, is Pigment Yellow 74, shown in Fig. 4*b*.

The positive and negative ion LDMS mass spectra for the yellow pigment from the older C80 pigmented ink printer, shown in Fig. 5, are similar to those shown in Fig. 4. The positive and negative ion spectra show the ionized molecule (positive and negative), fragment ions, sodium adduct ion, etc. that are identical to those seen for Pigment Yellow 74 in Fig. 4. However, Fig. 5 contains additional peaks, notably the peak at *m/z* 481 in the positive ion spectrum, a substantial peak at *m/z* 435 in the negative ion spectrum, and a high mass negative ion peak, *m/z* 893, as well. These peaks may all represent a single species. While there is a strong *m/z* 435 peak in Fig. 5*b*, there is no corresponding peak in the positive ion spectrum, suggesting that it represents an anionic component to the ink. There is a negative ion formed with an *m/z* value of 893, almost twice that of 435—actually it is 23 Da higher than (2×435). Assuming that 435 represents a singly charged anionic compound, then *m/z* 893 could be of the sodium-bound dimer $\{(X^-)_2(Na^+)\}^-$, consistent with the presence of a negatively charged molecule with a high relative abundance in the ink. The analogous ion in the positive ion spectrum would have one negative charge and two Na^+ ions, and is observed at *m/z* 481. Thus, it appears that the additional three peaks are consistent with the presence of a charged compound with an anionic *m/z* value of 435. Pigment Yellow 74 is an interesting pigment—"one of the cheapest organic yellows with properties on the borderline of necessary fastness—no one loves it—everybody needs it" (21). Several patents have discussed the addition of yellow dyes to Pigment Yellow 74 to form a dispersion for use in inkjet printer inks (22,23). Anionic dyes such as Direct Yellow 132, Acid Yellow 23, and Direct Yellow 86, have been suggested in the patent literature as being suitable yellow dyes to make dispersions with Pigment Yellow 74, because they have structures similar to that of the pigment, allowing them to be physically adsorbed onto the pigment particles (22,23). Unfortunately, none of the anionic dyes discussed in the patents would form a molecular anion of *m/z* 435. There is no obvious yellow anionic dye that matches this *m/z* value.

When TLC is performed with most pigmented inks, the pigment does not move on the TLC plate. However, in the case of the yellow ink from the C80 printer, a yellow band separates from the immobile pigment band. The experiment was repeated using paper instead of a TLC plate, and a yellow band, possibly representing a dye, was extracted off the yellow pigment. When analyzed by LDMS, the yellow "dye" that moved exhibited an *m/z* value of 435, and was present only in the negative ion spectrum. This reinforces the assignment of *m/z* 435 as representing an anionic compound. While assigning *m/z* 435 (and other peaks) as representing

a single dye is an obvious option, we have yet to find a specific yellow dye as a match. The peak at *m/z* 435 behaves as though it is anionic, and most anionic dyes contain sulfonate groups. If Pigment Yellow 74 were sulfonated (replace a H atom with an SO_3^- group), this would yield an anion with an *m/z* value of 465, which is 30 Da too high. Instead of replacing an H (−1 Da) with a sulfonate group (+80 Da), a sulfonate could replace a group with an atomic mass of 31, which would yield the correct *m/z* value of 435. In Pigment Yellow 74, there is a methoxy group (OCH_3) that weighs 31 amu. This substitution may be a possibility, but at this point only a conjecture. Thus, while the presence of another compound in the yellow ink has been established, its identity has not. Its presence distinguishes between the two printers.

The results presented in Figs. 1–5 show that LDMS can be used to detect and identify the pigments used in pigmented ink printers. The results also reinforce the concept noted earlier, in a study of pigmented pen inks (8), that while an ink may be "pigment based," it may still have one or more dyes present. In our studies with pigments encountered from a variety of sources, we now routinely do TLC analysis of all available ink samples, to determine if any of the pigmented ink samples contain dyes as well. Such information can be useful to have before attempting to interpret a spectrum. Also, if the pigment and dye can be separated, each can be analyzed by LDMS.

Analysis of Inkjet Printed Documents—A First Step

The goal of this work in analyzing inkjet printed documents is to be able to collect chemical information that might connect a questioned document to a specific type of printer. This involves determining if the document came from a dye or pigmented ink printer, assessing the number of colorants present (number of inks used), and determining the chemical identity of the dyes/pigments. This challenge is very different than anything performed before using LDMS, because pen strokes and automobile paint chips usually contain a single colorant. If an inkjet printed questioned document such as a color forgery is subjected to LDMS analysis, every sample location irradiated by the laser will likely contain hundreds of inkjet printed spots.

When starting not with the pure printer inks, but a printed document, how could one characterize the printer used in terms of the number of pigments (cartridges) used and their chemical identity?

When initially approaching the challenge, trying to determine how a CMYK printer uses its inks to create colors, a file was found on the Internet depicting the visible light spectrum (24). It was printed using the Epson C88+ printer. This generated a continuously changing gradient of printed "colors" from red through violet. The initial plan was to collect LDMS mass spectra across the range of colors, and identify the color components used at each point. The decision was made to collect spectra from 12 locations, equally spaced between the red end and the blue end, and to consider if and how we could determine, from the data, the number of inks used by this particular printer (which we knew to be 3, plus black, which is usually not used in printing color images [25]).

With a "stock" sample containing a full color spectrum to work with, the question remained of how to obtain LDMS mass spectra and how to present the results. One very important variable is laser power. At each location across the "visible spectrum document," one might work with a different laser power to get the "best" mass spectrum. Rather than vary power for each region/color, we chose to instead take preliminary spectra across the range of colors, find an intermediate laser power that yielded acceptable spectra for all colors/locations, and maintain that constant power for all of the mass spectra obtained. (To put this in context, all of the spectra shown in the first five figures were obtained using different laser powers, because the desorption/ionization efficiencies of each pigment is different.) There is always the possibility that, if the power is too high, some mass spectral peaks may become saturated, and if the power is too low, some components may remain undetected, so we were sensitive to these issues. It was decided that the relative intensities of mass spectral peaks would then be graphed versus "sample color" to get some idea of how the primary printer colors (CMY) were used. The mass spectral peaks are presented in terms of relative intensity (RI), so there is always a peak assigned a RI value of 100. Our experiences with analyzing pigments suggest that all pigments do not undergo the desorption/ionization process with equal efficiency; some can be detected more easily (at lower power) than others. This means the intensities do not directly correlate with the relative amounts of the pigments used, but do show which inks are used to create different colors.

Twelve positive ion mass spectra, one for each of the selected color regions of the color spectrum document, were obtained. The results were disappointing. Copper phthalocyanine, the cyan pigment, can be very efficiently detected in the LDMS experiment at low laser power, and its presence dominated most of the spectra. For spectra where the cyan pigment did not give the most intense mass spectral peak, an unidentified low mass peak (*m/z* 242) dominated. For many colors, we knew that other pigments were present, but they could not be efficiently detected in the presence of the copper phthalocyanine.

The experiments were repeated in negative ion mode, and the results were very different. The desorption/ionization efficiencies for the pigments used are comparable, when negative ions are generated, as opposed to positive ions. Certainly, they would be expected to differ, as considering the ionization step alone, ionization energies (to remove an electron from a molecule) are much different than electron affinities, which are the relevant quantity in forming a molecular anion.

Intensities of all mass spectral peaks were not graphed. We focused on the most intense peaks in each spectrum, excluding low *m/z* peaks that could not represent intact pigments. The negative ion data are summarized, for selected peaks, in Fig. 6—showing

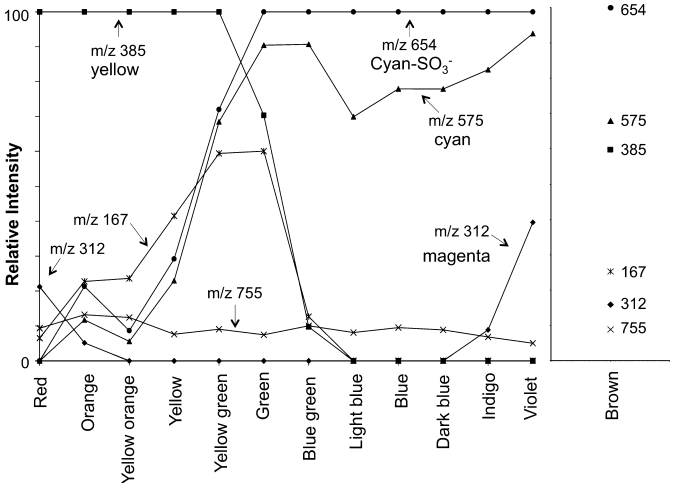

FIG. 6—*Variations in the contributions of pigments, as suggested by mass spectral peak intensities, from the Epson C88+ printer for printed colors across the visible spectrum—from red to violet. The box on the right shows data for LDMS spectra from a brown printed sample, as brown is not a color in the visible spectrum.*

how relative intensities of peaks, which we know to be related to the pigments used, vary from the red end of the spectrum to the violet end.

Several interesting and useful observations can be made. The peak at *m/z* 385 representing the yellow pigment is present at the red end of the visible spectrum, and is not used at all to form the colors at the blue end of the spectrum. The *m/z* 385 peak is the most intense in the red through yellow region, then makes a smaller contribution through the green and blue-green samples. We know that the *m/z* 575 peak represents the cyan pigment copper phthalocyanine. It is present at some level in all of the mass spectra except that corresponding to the red sample. The cyan is used to some extent in making most of the colors, and dominates the mass spectra for the colors from blue-green through violet.

The mass spectral peak at *m/z* 312 represents the magenta pigment. Note that it is only used at the ends of the color spectrum—to make red and to make violet. It is not used to create colors in the mid-spectral range, such as anything near yellow.

The relative intensities of some other mass spectral peaks are shown in Fig. 6. The *m/z* 575 and 654 peaks "track," and we have identified them as coming from the same ink cartridge (cyan). Peaks can correlate for a number of reasons. They could either come from the same cartridge, or they could be linked as coming from the same pigment (an ionized molecule and a fragment ion). The peak at *m/z* 167 is only present when *m/z* 385 is present, and data from Fig. 4 established that *m/z* 167 is a fragment ion of the anionic yellow pigment. Then there are peaks such as *m/z* 755; it is present in all spectra and does not correlate with any other peaks, so it likely represents a common component of the inks.

We have learned some very important facts from this experiment. First, it appears that, when working with a color document where the printer colors are mixed to form the perceived colors, negative ion LDMS is the preferred method for detection of all of the pigments, and, second, they can all be detected.

If the sample were an unknown, perhaps a counterfeit passport that was being analyzed, data could be collected to construct a graph similar to Fig. 6. One would try to find regions of the document that represent different colors—such as red, green, or blue printed text, a yellow shirt in a photograph, different shades of blue or green, etc. By collecting negative ion LDMS spectra and ordering them in terms of the visible spectrum, one may be able to start to connect *m/z* values with ink cartridge colors. If a mass spectral peak is present in blue and violet colors, it's probably not representing a yellow pigment. The data shown in Fig. 6 can be used to show how at least one printer creates colors from the available inks, which, for low-cost printers, are typically CMYK (with black not commonly used in creating color prints). If this were a true unknown and the color associated with each mass spectrum was known, one could correlate *m/z* values with possible pigment colors.

The visible light spectrum picture that was analyzed by LDMS does not contain all of the colors that could be encountered in a color print. Important colors such as brown are not represented. A photo that contained a brown region was printed using the C88+ printer, and was analyzed by negative ion LDMS. The contribution of the pigments to form brown, as suggested by the mass spectral peaks, is shown at the right side of Fig. 6. There is no location in the "visible spectrum" data where yellow (*m/z* 385), cyan (575, 654), and magenta (*m/z* 312) pigments are used, as they are in this region, to form brown.

Finally, it may be useful to comment on some relevant aspects of color. If a file is downloaded from a computer, the Internet, or a digital camera, the colors are usually encoded in three channels—red, green, and blue (RGB). Your eyes also encode in this way—responding to the relative amounts of red, green, and blue in the light that illuminates your retina. Computer and television screens most often use the RGB format for generating colors from individual pixels illuminated on the screen. Red, green, and blue are known as the additive primary colors. By mixing these colors two at a time, the additive secondary colors magenta, cyan, and yellow are formed. When using them to paint, print, or dye fabric, they can be considered as the subtractive primary colors, as each absorbs a portion of the visible spectrum, and reflects the light we see.

Together, computers and printers accomplish a substantial color-management challenge in converting RGB information from a digital file to a CMY format in a printer, referred to as a one-to-many mapping problem (25).

Current color printing technologies can use 30 or more inks or color sets (25). Some common color layouts that have gone beyond CMY and CMYK include C2M2YK (cyan, medium cyan, magenta, medium magenta, yellow, black), C3M3YK, CMYKOR (OR = orange, red), CMYKGO (GO = green, orange), and CMYKRGB (25). For each printer, algorithms have been created to map color usage from the original RGB computer file to the ink set available. Graphical analyses of how the available colors are used to create the desired colors, such as Fig. 6, provide insights into how this is accomplished.

Obviously, we have begun here with the analysis of regions of a color-printed document that contain pigments that we have already characterized. The challenge is more complex when the printer uses a larger number of (unknown) inks. This is beyond the scope of this particular paper but will be addressed in the future.

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References

1. Allison J. Ink analysis using UV laser desorption mass spectrometry. In: Blackledge RD, editor. Forensic analysis on the cutting edge. Hoboken: Wiley Interscience, 2007;57–77.
2. Grim DM, Siegel J, Allison J. Evaluation of desorption/ionization mass spectrometric methods in the forensic applications of the analysis of inks on paper. J Forensic Sci 2001;46:1411–20.
3. Grim DM, Siegel JA, Allison J. Evaluation of laser desorption mass spectrometry and UV accelerated aging of dyes on paper as a tool for the evaluation of a questioned document. J Forensic Sci 2002;47:1265–73.
4. Grim DM, Siegel J, Allison J. Does ink age inside of a pen cartridge? J Forensic Sci 2002;47:1294–7.
5. Dunn JD, Siegel JA, Allison J. Photodegradation and laser desorption mass spectrometry for the characterization of dyes used in red pen inks. J Forensic Sci 2003;48:652–7.
6. Grim DA, Allison J. Identification of colorants as used in watercolor and oil paintings by UV laser desorption mass spectrometry. Int J Mass Spectrom 2003;222:85–9.
7. Grim DM, Allison J. Laser desorption mass spectrometry as a tool for the analysis of colorants: the identification of pigments used in illuminated manuscripts. Archaeometry 2004;46:283–99.
8. Papson K, Stachura S, Boralsky L, Allison J. Identification of colorants in pigmented pen inks by laser desorption mass spectrometry. J Forensic Sci 2008;53:100–6.
9. Le HP. Progress and trends in inkjet printing technology. J Imaging Sci Technol 1998;42(1):49–62.
10. Epson America, Inc. Epson durabrite inks: technical brief. 2004; http://ftp.epson.com/pdf/sc80__/sc80__db.pdf (accessed November 26, 2008).

11. WIR_Epson3rdParty2007_09_11.pdf, http://www.wilhelm-research.com (accessed November 26, 2008).
12. Cunningham E. Pigmented inks for inkjet: have they arrived? American Ink Maker 1999;77(2):36–40.
13. Nakamura H, Miyabayashi T, Yatake M, Komatsu H, inventors. Seiko Epson Corporation, assignee. Microencapsulated pigment, production process therefor, aqueous dispersion and ink jet recording ink. US patent 7,074,843 B2. July 11, 2006.
14. Yamazaki S, Yamamoto Y, inventors. Seiko Epson Corporation, assignee. Image printing using print quality enhancing ink. US patent 6,863,374 B2. March 8, 2005.
15. Exclusive Canon bubble jet printer technologies herald new era in photographic printing. Business Wire. 1997 Jul 14, http://findarticles.com/p/articles/mi_m0EIN/is_1997_July_14/ai_19578798 (accessed November 26, 2008).
16. Musselman SW, Chandler S. Wetting and absorption of acetylenic diol-based nonionic surfactants on heterogeneous surfaces. Colloids Surf A: Physicochem Eng Asp 2002;206:497–513.
17. Pedrosa JML, Bradley M. A high-throughput and design of experiment mediated optimization of pigment-based ink formulations. Pigment Resin Tech 2008;37:131–9.
18. Herbst W, Hunger K. Industrial pigments: production, properties, applications, 2nd edn. Weinheim: VHS, 1997.
19. Santimauro JF. An introduction to copper phthalocyanine pigments. Dyestuffs 1960;43:158–63.
20. Stachura S, Desiderio VJ, Allison J. Identification of organic pigments in automotive coatings using laser desorption mass spectrometry. J Forensic Sci 2007;52:595–603.
21. Brochure EVP1706e, The response to highest demands! BASF pigments for mixing systems, http://www.basf.com/pigment (accessed November 26, 2008).
22. Yokoyama M, Takeuchi H, Tanaka H, Maruyama K, Kanazawa K, inventors. Mitsubishi Chemical Corporation, assignee. Ink-jet recording liquid and process for producing the same. US Patent 6918955. 2005 Jul 19.
23. Randler R, Rohr U, Geisenberger J, Baur R, Macholdt H-t, Menzel H, inventors. Clariant GmbH, assignee. Water based colorant preparations, US Patent 7008475. March 7, 2006.
24. http://www.phantasmcs.com/images/manual/faq/gradient-same-colour-1.png (accessed November 26, 2008).
25. Chen Y, Berns RS, Taplin LA, Imai FH. A multi-ink color separation algorithm maximizing color constancy. Proceedings of the 11th Color Imaging Conference: Color Science and Engineering Systems, Technologies, and Applications; November 3–7, 2003; Scottsdale, AZ. Springfield, VA: Society for Imaging Science and Technology and Society for Information Display, 2004;277–81.

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