Introducing state-of-the-art forensics into instrumental analysis laboratory:

detection of document forgery with laser desorption/ionization mass spectrometry

Igor A. Kaltashov, Kenyon Kowalski, T. Ryan Sullivan, Alyssa Marsico and Nicholas DeGraan-Weber

Department of Chemistry, University of Massachusetts-Amherst, Amherst, MA
ABSTRACT

Forensics has long been viewed by chemical educators as a field with great potential as far as providing inspiration for modifying chemistry laboratory curriculum and enhancing students’ learning experience at different levels. While most experiments are based on adaptation of laboratory procedures routinely used in criminalistics, very exciting (but frequently overlooked) opportunities are presented by state-of-the-art analytical technologies that are available on university and college campuses, but have not yet become commonly accepted tools in the armamentarium of forensic analysis. We illustrate this using as an example laser desorption/ionization mass spectrometry (LDI MS), a technique which has been actively evaluated in recent years in forensic community as a tool to detect forgery in various printed and hand-written documents. Two possible uses of this technique in the undergraduate laboratory are described, one focusing on fraudulent alteration of a personal check, and another focusing on detecting forgery in a printed document. Both experiments are open-ended, in that the initial findings invite additional questions and encourage further work. As such, these themes can be used not only as modules in analytical or instrumental laboratory, but also as templates for more in-depth work, such as independent study by chemistry majors and advanced high school students.
INTRODUCTION

The continuing transformation of our approaches to teaching chemistry and other science disciplines aims at fostering active and independent student engagement, a goal that requires experimentation with teaching methods. One of the important findings of the past two decades is the realization of the role played by the “real world” context and the way it connects to the concepts learned both in the classroom and the laboratory. Students commonly find participation in the context-driven tasks interesting and productive, and this positive learning experience encourages much greater levels of engagement with the taught material both in the classroom setting and as independent learners. One of the most effective ways to achieve these goals is based upon placing chemistry within a societal context, using themes such as health, environment and forensics. While the first two themes provide the context to which students can readily relate through their own experience, or as members of both local and global communities, forensics (fortunately) lies outside of the everyday experience of most students. Nevertheless, this field is frequently viewed by adolescents and young adults with a good measure of fascination, a phenomenon that can be attributed to the influence of the mass culture (the so-called CSI effect). It is therefore not surprising that forensics has long been viewed by chemical educators as a teaching tool with great potential as far as providing inspiration for modifying chemistry curriculum and enhancing students’ learning experience both in the lower and upper level courses (including chemistry for non-majors and for liberal arts students).

An impressive array of experiments have been already published for the upper level chemistry laboratories (quantitative analysis and instrumental analysis) that emulate forensic work focusing on measuring blood alcohol level, detection and identification of drugs of abuse, analysis of trace evidence collected at the crime scene, arson investigation, and forensic DNA analysis. The vast majority of these experiments are based on adaptation of routine procedures that are already used in forensic laboratories around the country and the globe. However, forensic analysis is a very dynamic field, and even brief review
of current literature yields a range of state-of-the-art techniques that show great promise for solving challenging problems in criminalistics, but have not yet become commonly accepted as routine analytical tools within the law enforcement and legal communities. Analytical instrumentation utilized in such pilot studies is frequently available on college campuses in both teaching and research laboratories, which not only allows the new cutting edge forensic technologies to be incorporated in the chemistry curriculum, but also provides a unique and exciting opportunity for students to make meaningful contributions to the ever growing arsenal of forensic analysis while learning important chemistry concepts.

Mass spectrometry (MS) is an example of an analytical technique that enjoys growing popularity within the forensic community, with emerging applications ranging from identification of counterfeit drugs\textsuperscript{10} to detection of explosives.\textsuperscript{11} A wide range of the state-of-the-art MS instrumentation is now widely available in research facilities in all major universities and many smaller colleges, while the growing availability of relatively inexpensive mass spectrometers has already started a trend of incorporating MS in the experimental arsenal of undergraduate teaching labs. Although the exact statistics are not available, GC/MS probably still remains the most popular teaching tool worldwide forty years past its initial introduction to an analytical/organic undergraduate laboratory by M.L. Gross and his colleagues at the University of Nebraska-Lincoln.\textsuperscript{12} Increased emphasis on life sciences in chemistry research and instruction in recent years paved the way for adoption of other MS techniques in teaching laboratories, such as matrix-assisted laser desorption/ionization (MALDI) MS.\textsuperscript{13} While the vast majority of published laboratory exercises aim at probing composition and structure of biopolymers, MALDI MS also enjoys popularity as a potent analytical tool for synthetic polymers and other macromolecules of abiotic origin.\textsuperscript{14} On the other hand, the utility of MALDI MS,\textsuperscript{15} its sister technique laser desorption/ionization (LDI) MS,\textsuperscript{16} and other \textit{in situ} ion desorption MS techniques\textsuperscript{17} in forensic analysis has been recently evaluated by several groups with a particular emphasis on document forgery detection, although neither one has become a routine tool in fraud investigations as yet.
Document forgery is an unfortunate byproduct of the human ability to produce written documents and is likely to be as old as the writing itself (with the earliest known examples dating back several thousand years ago\textsuperscript{19}). It has been noted that no other instrument of crime is as prevalent in modern society as documents,\textsuperscript{19} with examples ranging from rather mundane falsification of checks and receipts to high-stake forgeries of wills.\textsuperscript{20} Numerous highly publicized examples of suspected forgery are truly captivating due to either bizarre circumstances (e.g., the case involving two different forgeries of the same document presented by the two conflicting parties\textsuperscript{21}), astronomical price tag (e.g., the case of the forged will of the late Hong-Kong billionaire Nina Wang\textsuperscript{22}), or enormous societal impact (e.g., ink examination in the diary that eventually led to the downfall of vice-president Spiro Agnew in 1973\textsuperscript{23}). Above and beyond such high-profile celebrity cases, students can relate to the societal impact of document forgery through recently publicized instances of falsifying foreclosure documents in the wake of the 2008 real estate bubble burst.\textsuperscript{24}

Presentation of the forgery case studies or generating mock falsified documents for laboratory work is easy and avoids the unneeded mental discomfort associated with presenting murder cases and other violent crimes,\textsuperscript{25} which may easily unnerve sensitive students and negatively impact the learning process.

Despite this appeal of document forgery as a subject of laboratory examination in upper level chemistry courses, only one such experiment has been presented in chemical education literature in the past twenty five years. This exercise, published in 1991, involves a now-classic fingerprinting of pen ink, which relies on solvent extraction of dyes followed by their separation and identification by thin layer chromatography (TLC),\textsuperscript{26} a process that emulates the forensic procedure which makes use of the extensive pen ink library maintained by the U.S. Secret Service.\textsuperscript{27} Despite being featured in one of the CSI episodes, this procedure is unlikely to generate much awe among the modern technology-savvy college students, and has been deemed more appropriate for the “8+” audience by Toys’R’Us, who markets the TLC-containing “CSI Ink Analysis Kit” to “everyone who wants to become a detective” at a bargain price of $9.97. Despite this trivialization of the classical analytical procedure, forensic document examination in general still has a
great potential in sparking students’ interest and imagination. Coupled with the dramatic progress in the field of surface analysis made in the past two decades and the continuous incorporation of many of these technologies into the arsenal of forensic science, it prompted us to start re-evaluation of the educational value of document examination/forgery detection in analytical and instrumental laboratories. In this report we present several possible uses of LDI MS (focusing on fraudulent alteration of a personal check and on detecting forgery in a printed document) in the undergraduate chemistry laboratory. One intriguing conclusion of this work is that these experiments are open-ended, in that the initial findings invite additional questions and encourage further work. As such, these themes can be used not only as modules in analytical or instrumental laboratory, but also as templates for more in-depth work.

EXPERIMENTAL METHODS

**Preparation of mock forged documents.** A variety of high-resolution blank check templates can be downloaded from the web (e.g., [http://www.psdgraphics.com](http://www.psdgraphics.com) offers free downloads of a high-resolution JPEG image). Any graphic software (such as Adobe Illustrator or Corel Draw) can be used to place a mock address on the blank to give it the appearance of a real check. Two different black pens can be used to create the initial text ("original" ink) and a later addition ("suspect" ink), as shown in Figure 1A. The following two generic gel pens were used in this work, a Papermate gel pen (used as the original pen) and a Sharpie felt tip pen (the suspect pen). A mock forged receipt can be prepared by typing a text with an inkjet printer, followed by addition of new text and/or symbols later using a different printer (Figure 1B). The following inkjet printers/black inks were used in this work: Epson Workforce 435/T1241 124 Black; Hewlett Packard Photosmart C5550 all-in-one printer/HP 74xL black ink cartridge CB336W; Kodak ESP Office 2170/Kodak 30 Black; and Canon PIXMA MX860/PGI-220BK.

**LDI MS analysis of mock forged documents.** An Autoflex-III (Bruker Daltonics, Inc., Billerica, MA) MALDI/time-of-flight (TOF) MS was used for all small-scale measurements. The samples of both pen and
inkjet printer inks on paper were collected by cutting out small (ca. 2x2 mm) pieces of either document and attaching them to the sample stage using a double-sided Scotch tape. No chemical treatment of the samples was needed, and no MALDI matrices were applied to the samples. Imaging measurements were carried out using Autoflex Speed MALDI TOF/TOF (Bruker Daltonics, Inc., Billerica, MA) mass spectrometer, where a large piece of document was attached to a 3” × 5” stainless steel target. External calibration was used in all measurements.

**Hazards.** No specialty chemicals or solvents were used in the entire procedure, thereby eliminating any possibility of students’ exposure to hazardous materials. However, the MALDI TOF MS instrument employs a UV laser for ion production and high voltage for ion acceleration. Although the instrumental design eliminates the operator’s exposure to either laser radiation or high voltage under normal operating conditions, caution must be taken in order to prevent any possibility of electrical shock or eye exposure to the laser beam by following the instrument manufacturer’s operating instructions. Students must wear protective eyeglasses and be closely supervised by a qualified person at all times.

**RESULTS AND DISCUSSION**

*Pen ink analysis: detection of a personal check forgery.* Dyes used in pen inks are small organic molecules that absorb light in the visible region; they also exhibit strong absorption in the near-UV region (this is due to the presence of multiple aromatic rings with significant degree of conjugation\textsuperscript{17c, 19}). Because of the strong UV absorbance of dyes, their analysis does not require application of MALDI matrices, whose purpose is to absorb the laser radiation and use this energy to eject/ionize other molecules to the gas phase. This allows the dyes to be desorbed directly from the paper surface upon irradiation with a laser beam, and use the resulting mass spectra to identify specific dyes present in a particular ink preparation or blend.\textsuperscript{16b-d} LDI mass spectra of two ink samples from a mock forged check (“original” and “suspect” ink, Figure 2A and B, respectively) contain some common features (\textit{e.g.}, peaks 1, 2 and 4). Based on the
measured ionic masses, these peaks were assigned as methyl violet B, Victoria pure blue BO, and copper (II) phthalocyanine, respectively. These dyes are commonly found in ball point and gel pen inks\textsuperscript{17c,28} (their chemical structures are shown in Figure 3). Additional confirmation of the peak assignment comes from close examination of the isotopic distributions of ion peaks (see insets in Figures 2A and B). While isotopic distributions of small (below 1,000 Da) organic molecules containing carbon, hydrogen, nitrogen and oxygen atoms are expected to be monotonic, presence of elements such as chlorine, as well as some transition metals give rise to convoluted isotopic distributions. A close match between the calculated isotopic distribution of copper (II) phthalocyanine and the measured one for peak 4 is another identity proof for this ink component. The most significant difference between the two spectra is the cluster of peaks in the m/z range 470-500 (labeled 3 and 3'), which are present only in the mass spectrum of the original ink. The ionic mass of peak 3 allows it to be assigned as crystal violet, another common dye, while 3' is likely to represent a fully methylated version of this molecule (a common chemical modification in dyes that converts, \textit{inter alia}, methyl violet B to Victoria pure blue BO, see Figure 3).

This ability of LDI MS to provide a clear distinction between the original and the suspect inks not only allows the document examiner to prove that two different inks were used in a single document, but also to establish which specific entries were made with a particular pen. Furthermore, an LDI mass spectrum collected from a document spot where the marks left by the original and the suspect inks overlap (Figure 2C), exhibits the entire collection of dyes 1, 2, 3, 3' and 4. However, the relative abundance of peaks 3 and 3' is very low compared to 4 (less than 1:30), while this ratio exceeds 1:1 in the mass spectrum of the original ink. This observation confirms that the writing done with the suspect ink was added to the check later, a feature that can be used for establishing chronological order of placing entries in disputed documents.
Inkjet printer ink analysis: detection of forgery in a printed document. The MS analysis of colorants in pen ink described in the preceding section is relatively straightforward in that dyes are relatively small organic molecules and strong UV chromophores, two features which allow them to be easily observed in LDI mass spectra. Examination of documents produced with inkjet printers is more complicated, as the colorants used in inkjet inks are pigments, which are insoluble sub-micron particles that often require dispersants (surfactants and polymers) to obtain stable formulations and prevent the fine pigment particles from settling.\textsuperscript{29} Although most pigments, just like dyes, are strong UV chromophores, their large size (commercial inkjet inks have pigment particle diameters that range from 0.1 to 0.2 µm\textsuperscript{30}) frequently prevents generation of analytically useful ionic signal. Instead, pigments in LDI MS measurements play the same role that matrices do in MALDI MS, \textit{i.e.} they convert the energy of laser radiation to other forms of energy, leading to ionization and ejection of other ink components from the surface.

LDI MS analyses of samples cut off from documents printed with four different inkjet printers generate very distinct mass spectral patterns (Figure 4). The main feature of each spectrum is the presence of wide distribution(s) of peaks spaced by 44 Da, which indicate the presence of polyethylene glycol (PEG) in each ink sample.\textsuperscript{14} This is hardly surprising, since PEG is a common component in many printing ink formulations, which prevents ink drying and enhances jetting performance. What is interesting (and was certainly unexpected), is the fact that all four inks whose LDI mass spectra are shown in Figure 4 appear to contain different PEG blends. The distinction among these inks can be made based upon average molecular weight of PEG blends (\textit{e.g.}, compare panels C and D in Figure 4), or their composition (\textit{e.g.}, compare binary blend in panel E to single-mode PEG distributions in panels B-D).

Even when the average molecular weights of the PEG components of the inks are very close to each other (\textit{e.g.}, panels B and C in Figure 4), a distinction between them can be made based on the composition of the end groups. Indeed, close examination of masses of PEG ions in LDI mass spectra of all four inks (insets
in Figure 4) reveals very significant differences. The mass of each PEG ion is a sum of the mass of the chain, end groups, and a cation (usually either sodium or potassium):

\[ M_{\text{PEG}^+} = n \cdot M_{\text{C}_2\text{H}_4\text{O}} + M_{\text{end groups}} + M_{\text{cation}} \]  

(1)

While the first term in this equation gives rise to the periodicity of the ionic signal (by generating equidistant peaks separated by 44.0 Da), the two other terms are responsible for the offsets of these ladders with respect to one another, as well as for appearance of multiple ladders within the same m/z region (a feature that is particularly pronounced in the mass spectrum shown in Figure 4D). Since Na\(^+\) and K\(^+\) (23.0 and 39.0 Da, respectively) are usually the only two ubiquitous metal ions that act as cationizing agents for PEG, the third term in equation (1) alone cannot explain the observed variation in masses of PEG ions, and one needs to consider the second term (end group mass).

Most of the commercial ink formulations are proprietary, and information on composition and chemical structure of polymers used as dispersants is not readily available, making the unequivocal assignment of the peaks in mass spectra shown in Figure 4 impossible. Although a significant volume of information on ink composition can be found in patent literature, one should be aware that some critical “details are often not mentioned in the patent disclosures” and “patent law does not prevent the inventors, or more accurately the inventors’ company intellectual property lawyers, from including in the patent disclosure large volumes of suboptimal alternative approaches that one may cynically believe are meant to slow down competitors by providing false leads.”  

30 Even a brief search of patent literature reveals a great variety of end groups that are used in preparation of PEG-based dispersants for inkjet ink formulations (several representative examples are shown in Figure 5), and some of these structures match the measured masses of polymers in the LDI mass spectra of the ink samples (for example, the low molecular weight distribution of ions in Figure 4E matches the calculated masses for structure I in Figure 5,
polyoxyethylene lauryl ether, which is a component of many commercial dispersants, such as Nikkol DLP-10<sup>30</sup>.

However tempting it might be to obtain PEG assignment based on these mass matches, one must be aware of the limitations of this procedure. First, there may be two or more different chemical structures that would generate a nominal mass match for a single PEG distribution. For example, polyoxyethylene lauryl ether would be indistinguishable from structure VII in Figure 5, glycolic acid ethoxylate lauryl ether, another popular polymer additive (although these two polymers can be distinguished using high resolution mass measurements). The second (and perhaps more significant) problem is that the actual number of PEGs used as dispersants is significantly larger than those represented in Figure 5, and continues to grow; in addition to the linear structures, there are also branched polymers used as surfactants and dispersants in ink formulations (see, for example, U.S. patent 7,160,376 B2), and their distinction from linear polymer chains on the basis of a mass measurement alone is impossible.

Therefore, instead of identifying inkjet ink components (as was the case with the pen ink considered earlier), one should focus on obtaining and comparing the patterns of PEG ion distributions in LDI mass spectra. Not only can these patterns be used as fingerprints to establish the fact that two different printers were used to generate the suspicious printed document (Figure 1B), but matching them against the library of inks from different manufacturers (such as the one shown in Figure 4) may allow one to establish the brands of the printers used in document preparation without the need for extensive chemical characterization of the ink.

*Chemical imaging with LDI MS: towards non-destructive forensic analysis of hand-written and printed documents.* The analyses described in the preceding sections have a significant disadvantage from the legal point of view in that they are destructive: a small piece of paper (ca. 2x2 mm) is cut from a document prior to LDI MS measurements, and the mass spectra are acquired from a few spots within a stroke.
Ideally, evidence destruction (which is also occurring when the document analysis is carried out using the commonly accepted TLC-based technique) should be avoided, and the continuous advances in using MS instrumentation as imaging tools may allow this goal to be achieved (at least for documents of modest size). The small-scale nondestructive LDI MS analyses were carried out in this work using the imaging capability of modern state-of-the-art MALDI TOF mass spectrometers. While such instrumentation remains relatively expensive and is unlikely to become a part of the experimental arsenal of teaching laboratories any time soon, many academic mass spectrometry facilities do have imaging MALDI MS, which might be used for advanced projects by undergraduate chemistry majors. A variety of experiments could be implemented as a follow-up to the work presented in the previous sections. For example, Figure 6 illustrates how alteration of hand-written documents can be detected by producing molecular images of the surface of a piece of paper with questionable writing (“8” had been added right before “100” imitating the handwriting style and using the pen with the ink indistinguishable from that used for the original writing). The chemical image of the surface was produced by rastering the sample under the stationary laser beam, such that a mass spectrum was acquired for every pixel. The resulting data array was converted to a two-dimensional signal intensity map of ions at $m/z$ 358 representing one of the most abundant dyes, methyl violet B (structure (1) in Figure 3). The dramatic signal intensity mismatch in Figure 6 provides a clear indication that the abundance of methyl violet B is significantly higher in the first hand-written number compared to the rest of the entry, proving that different inks were used to enter “8” and “100.”

Since a complete mass spectrum is acquired for each pixel in chemical imaging experiments, the students can extract multiple maps (representing different dyes) from a single data set. Superposition of such intensity maps can be used to establish the chronological order for overlapping entries where visual inspection alone is not sufficient, e.g. to reveal “signature over print” vs. “print over signature” orders in disputed signed documents, where the order of placing the entries is uncertain and cannot be determined
by visual inspection (similar to the case shown in Figure 1B, where the “legitimate” text should be below the layer of pen ink at all intersections, while all added text will be inevitably placed over the pen strokes of the signature). An example of such analysis is presented in Figure 7, where a text was printed over handwriting, and this order is readily established by observing the ionic trace at m/z 1209 (representing PEG molecule unique for the printer ink) overlaid on top of the ionic trace for m/z 358 (representing methyl violet B, an ink dye not present in the printer ink).

Students’ interpretation of the experimental data and discussion of the follow-up work and further improvements of the analyses. One of the benefits of incorporating the LDI MS-based forensic experiments focused on forged document analysis in the undergraduate laboratory is that it allows the material to be explored at multiple levels and with a significant degree of flexibility. For example, students in the lower-level analytical laboratories may focus on the analysis of pen inks, where complete identification of the dyes is possible based on the mass measurement alone. Above and beyond the mass measurements and their use in organic molecule identification, these experiments provide a perfect opportunity to explore the concept of isotopes, and the use of isotopic distributions in chemical analysis.

More advanced courses, such as instrumental analysis, may consider analysis of inkjet ink, where explicit assignment of all ink components is not feasible, but the spectral features can nonetheless be used to achieve the forensic objectives. This work would be ideally suited for introducing students to advanced concepts in analytical chemistry, such as spectral database/library searches and chemometrics. Analysis of pen ink can also be carried out at the advanced level, but the questions to be addressed by students would be more complex than simple correlations of the mass and the chemical structure of dyes. For example, one may explore the reasons for the slight deviation of the measured isotopic distribution of peak 4 from the calculated isotopic distribution of copper (II) phthalocyanine (inset in Figure 2B). The following three possibilities should be considered: (i) inadequate ion statistics, (ii) partial in situ Cu^{2+}
reduction, giving rise to a mixture of singly charged ions with different number of protons, and (iii) deviation of the $^{65}\text{Cu}/^{63}\text{Cu}$ ratio in the dye product from the commonly accepted one (former NIST SRM 976). It is the latter possibility that is the most exciting as far as forensic applications are concerned (e.g., for the purposes of establishing sample provenance, etc.); however, the first two possibilities must be carefully evaluated prior to reaching any conclusions. Students may be asked if it is possible to distinguish variation of the $^{65}\text{Cu}/^{63}\text{Cu}$ ratio from that of $^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$ with MS, a perfect exercise for exploring the concepts of mass defect, mass resolution, etc.

All experimental data presented in this report were obtained by undergraduate and first year graduate students, who also played a very active role in planning the experimental work, interpreting/discussing the results and reflecting on various ways further experiments can be carried out. One outcome of such discussions was the examination of overlapping ink marks to establish the order in which various handwritten entries have been made (Figures 2C) and examination of mixed documents by establishing the pen over print vs. print over pen layers ordering (Figure 7). Another suggestion that resulted from these discussions related to the possibility of building a database of commercial inkjet inks (using both brand names and aftermarket products), similar to the extensive database of writing inks maintained by the U.S. Secret Service. Lastly, student participants expressed great interest in evaluating the feasibility of using LDI MS for dating documents by (i) analyzing “legacy” inks and (ii) investigating ink photodegradation processes as a result of its exposure to light. These suggestions open up exciting possibilities for planning follow-up work that can be carried out within the format of independent studies; apart from the obvious pedagogic value, it may be of interest to the law enforcement and legal communities (which, in turn, would further increase student motivation and engagement).

CONCLUSIONS
Introduction of the emerging methods of forensic analysis into undergraduate laboratory is a great way to enhance student engagement in the coursework by providing context that is viewed by most adolescents and young adults with fascination. Forensic analysis of documents (detection of suspected forgery) using LDI MS is a rapidly developing field, and availability of MALDI TOF mass spectrometers on many college campuses allows this work to be included in analytical and instrumental laboratories. Student access to the state-of-the-art imaging MS equipment can be used to evaluate the feasibility of using LDI MS for non-destructive analysis, a very attractive feature in the legal field where preservation of the evidence is highly desirable. All experiments presented in this report are open-ended, in that their completion invites further work, whose results may be of great interest to forensic professionals.

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**Figure 1.** Examples of mock forged documents that can be used for LDI MS analysis of pen ink (A) and inkjet printer inks (B). The two images on each panel show where alterations were actually done.
Figure 2. LDI mass spectra of the original and suspect inks from lines drawn on paper using Papermate gel pen (A) and a Sharpie felt tip pen (B). Panel C shows a mass spectrum collected from an intersection of the Papermate-drawn line and the line drawn with the Sharpie pen over it. Insets in panels A and B show calculated (bars) and measured (continuous lines) isotopic distributions of Victoria pure blue BO (species 2) and copper (II) phthalocyanine (species 4) cations.
Figure 3. Chemical structures of several dyes commonly used in ball-point pen and gel pen inks.
Figure 4. LDI mass spectra of the surface of white office paper obtained from ink-free regions (A) and from the text printed with Canon (B), Epson (C), Kodak (D) and HP (E) inkjet printers (see experimental section for specific inks). Outlays of panels B-E show detailed views of m/z regions 510-790 for each ink to emphasize the complexity of PEG ionic signals.
Figure 5. Chemical structures of several PEG-based dispersants of inkjet printer inks found in patent literature.
Figure 6. Left: a photograph of a piece of paper where “8” and “100” were hand-written next to each other using two different black pens with visually indistinguishable inks. Right: a chemical image of the surface of the paper showing the signal intensity map of ions at m/z 358 representing methyl violet B.
Figure 7. Top: a photograph of a text printed over a hand-written signature (executed with a pen). Bottom: a chemical image of the surface of the paper showing signal intensity maps of ions at m/z 1209 (green) representing PEG molecule (unique for the printer ink) and m/z 358 (yellow-orange) representing methyl violet B (unique for the pen).
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