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Analysis of writing inks on paper using direct analysis in real time mass spectrometry

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ABSTRACT

Ink analysis is central to questioned document examination. We applied direct analysis in real time mass spectrometry (DART MS) to ballpoint, gel, and fluid writing ink analysis. DART MS acquires the mass spectrum of an ink while it is still on a document without altering the appearance of the document. Spectra were acquired from ink on a variety of papers, and the spectrum of the blank paper could be subtracted out to produce a cleanly isolated ink spectrum in most cases. Only certain heavy or heavily processed papers interfered. The time since an ink is written on paper has a large effect on its spectrum. DART spectra change radically during the first few months after an ink is written as the more volatile components evaporate, but the spectra stabilize after that. A library-search study involving 166 well-aged inks assessed the ability to identify inks from their DART spectra. The aggregate success rate was 92%.

1. Introduction

Documentation is required in all aspects of modern society. Documents have therefore become a major tool for criminals. Questioned document examination is a broad field that includes the functioning of printers and copiers, handwriting examination, the physical structure and chemical makeup of paper, and the aging of documents. A universal aspect, however, is ink. Writing ink is particularly important because of the significance of signatures and handwritten records. Analysis of ink can determine whether writing has been altered, whether a document has been back dated, what the relative ages of ledger entries are, and the approximate age of the document [1]. A central aspect of ink examination is determining the formulation of the ink. Once the formulation of an ink has been identified, its production dates, geographic distribution, and prevalence can be determined [2,3].

The most common forensic methods for analyzing inks from documents are thin layer chromatography (TLC) and optical examination [4–9]. Optical examination is quick and nondestructive, and it is often sufficient for the relevant questions in a particular case, but it is useful only when a direct sample comparison can be made between the ink in question and reference samples. A difference observed by optical examination is usually a firm indication that the ink samples are not the same, although batch-to-batch variations, changes from ink aging, and possible interferences must be taken into account [3]. On the other hand, a match by optical examination implies only that the samples are similar. TLC provides more information about an ink, including limited formulation data. Ink analysis by chromatography has been growing since the 1950s [10] and is now a mature technique. TLC provides a stronger link between two matching samples than optical examination does, but the analysis is usually limited to the colored and fluorescent components of the ink [11]. Just as in optical examination, a collection of reference inks must be maintained, however recent work has been aimed at making the TLC analysis results more standardized and amenable to inclusion in a digital database [12]. A match between inks by TLC analysis does not prove that the inks are the same, only that they have similar formulas involving the same nonvolatile colored or fluorescent constituents [4,5].

Other analysis techniques have been successfully applied to inks, including high-performance liquid chromatography (HPLC) [13–15], capillary zone electrophoresis [15,16], X-ray fluorescence [15,17–19], surface-enhanced Raman spectroscopy (SERS) [20–22], and FT-IR spectroscopy [7,15,18,23,24]. These generally provide more compositional information than TLC does, and some of them lend themselves to computer-searchable libraries, so a

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reference collection of inks need not be maintained. The greater amount of information provides more characterizing features with which to identify or date inks [25]. Nevertheless, they have disadvantages. X-ray fluorescence is limited to elemental analysis. Some methods, like FT-IR spectroscopy, suffer from overlap of features from various ink (and possibly paper) components and so do not provide enough characteristic information to reliably distinguish similar ink formulations from one another [23]. Those that separate an ink into its components (i.e., HPLC, capillary zone electrophoresis) are slow and do not provide sufficient characteristic information on the components either for building a digital library or for reliably distinguishing ink formulations.

We have applied the mass spectrometry (MS) sampling interface called direct analysis in real time (DART) to the forensic analysis of inks because it provides detailed chemical information on inks, takes advantage of the power of modern computer databases, and is well suited to ink analysis [26,27]. DART MS samples ink directly from a document without altering the appearance of the document because no sample needs to be cut out, and it removes so little of the dyes and pigments that constitute the visible portion of the ink [27].

Conventional mass spectrometry has been used to analyze inks extracted from paper [28–30]. The resulting spectra are dominated by the ink dyes, which are the most abundant components of dry ink. The mass spectrometry results allowed individual dyes in an ink to be identified, but the inks studied could not always be differentiated from one another because many inks have nearly identical dye content [29,30]. Fortunately, DART detects many components other than dyes.

Less conventional mass spectrometry approaches other than DART have also been used to study inks. Both laser desorption mass spectrometry (LDMS) [31–37] and matrix-assisted laser desorption and ionization (MALDI) mass spectrometry have been studied [35,38]. Secondary ion mass spectrometry (SIMS) has also been tested [39–41]. All of these require removal of samples from the document or other evidence-altering preparations of the paper before it can be tested, and they all produce spectra that are dominated by the dyes. One additional technique which shares with DART the ability to analyze unprepared documents in the open air is desorption electrospray ionization (DESI) mass spectrometry. It has been used on ink on paper, and its spectra have peaks from both dyes and other ink components [42]. Unfortunately, DESI samples a specimen using a fine spray of solvent, so it could alter the document.

Since its commercial introduction in 2005, DART mass spectrometry has attracted substantial interest in the forensic community. It has been applied to the identification of counterfeit drugs [43,44], illegal drugs [45–48], drugs in urine [45,49] and plasma [50], chemical warfare agents [45], explosives [45], and arson accelerants [45,51].

2. Material and methods

The instrument used was a JMS-T100DART AccuTOF-D mass spectrometer (JEOL USA). This consists of a time-of-flight mass spectrometer with a DART 100 ion source. The DART source has been described in detail elsewhere [26]. The present method is similar to that used for a previous note on ink analysis [27]. In the present application, helium gas at 3.25 L/min passed through a hydrocarbon filter (Restek Corp.) and then into the DART discharge chamber where the needle electrode was held at −3500 V. This produced both helium ions and metastable (i.e., electronically excited) helium atoms. The gas then passed through the discharge and grid electrodes, which were at 150 V and 650 V, respectively, to prevent the passage of ions but allow passage of the metastable helium. The heater between these electrodes was set to 255 °C. This temperature helps evaporate material from the sample without discoloring the paper. After passing through the grid electrode, the hot, metastable-containing helium entered the open-air gap between the DART source and the mass spectrometer inlet orifice. This adjustable gap was set to 1.17 cm in length. The metastable helium ionized moisture in the room air in the gap, producing protonated water clusters, $(H_2O)_nH^+$. The sample to be analyzed was held in the helium stream approximately in the middle of this gap and the hot gas, metastable helium, and protonated water clusters combined to evaporate and ionize material from the sample. The ions were then swept into the mass spectrometer to be analyzed.

The ink-on-paper samples were held in a custom sample mount in which the paper sample wrapped around the rounded end of a metal support and was held on the support by a thin aluminum plate that exactly fitted over it. The plate had a 3.2 mm square hole, which defined the area exposed to the DART sampling stream. The support also had a hole in it that aligned with the hole in the cover plate. The tested area of the paper sample was therefore free standing. The sample mount was on the end of a short, pivoting arm that rotated the sample into position in the sampling stream so that all samples were reproducibly positioned in the same location during testing. The mount was electrically connected to the spectrometer inlet orifice. Fresh fingerprint residue is easily detected using DART, so gloves were worn when handling the samples.

The mass spectrometer was operated in positive ion mode. The inlet orifice (Orifice 1) was set at 20 V and 80 °C, Orifice 2 was 3 V, and the ion guide high-frequency voltage (Peaks Voltage) was 600 V. The low orifice voltages produced minimal fragmentation of the ions. As a result, the DART mass spectra were dominated by protonated molecules, $(M + H)^+$, where M is the parent molecule.

Most inks produce an immediate, strong pulse of ions when first positioned in the sampling stream, and the signal drops off after the first 10 or 20 s as the most volatile species diminish. Less volatile species, however, are still present after more than a minute. The spectra reported here consist of averages over the first 30 s of the observed signals. Spectra of the blank paper were acquired whenever ink-on-paper spectra were recorded, and the blank-paper spectra were subtracted 1:1 from the ink-on-paper spectra. Mass calibration was accomplished by recording the mass spectrum of a mixture of polyethylene glycols with an average molecular weight of 600 (PEG 600) in each data file. The mass scales for all spectra within the file were then calibrated using the PEG 600 spectrum. Once calibrated, the mass scale was accurate to approximately 0.003 u. This accuracy often allows elemental composition assignments to be made for individual spectrum peaks.

Centroided mass spectra were exported to the NIST Mass Spectral Search Program (Version 2.0) for library creation and searching. The NIST program records masses only to integer accuracy so the library tests do not take full advantage of the observed mass accuracy of the spectrum peaks. Library searches were done using the Quick Identity search with no limits on m/z or abundance ranges. Reverse searching was used for comparing the effects of paper, and forward searching was used for ink identification. A match factor of 999 corresponds to a perfect match between spectra.

All samples used in this study were prepared by drawing ink lines freehand on paper. The specific inks and papers used for each aspect of the study are given in Section 3.

3. Results and discussion

3.1. Effects of paper

How the paper on which an ink is written affects the DART mass spectrum was examined by comparing spectra of the same ink on