J13 Characterizing Writing Inks on Paper Using DART Mass Spectrometry

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The goal of this presentation is to provide details on how mass spectrometry with the new DART (direct analysis in real time) ion source may be used to differentiate and analyze inks on documents without altering the appearance of the document.

Ink analysis is typically limited to optical inspection and thin layer chromatography. Although these are often sufficient, mass spectrometry provides substantially more information. The DART ion source allows inks to be analyzed by mass spectrometry directly on the document. This approach to ink analysis will impact the forensic science community by providing a new method for rapidly analyzing inks that provides more detailed informa- tion than typical methods.

DART mass spectrometry provides a rapid, nondestructive method for the forensic analysis of inks on questioned documents. The DART ion source was introduced in 2005. It vaporizes and ionizes a small amount of material from the surface of a sample, such as a written document. The ions are then swept into and analyzed by a mass spectrometer with an atmospheric- pressure inlet. No sample preparation is required. The document is simply held in the sampling stream, which is open to the room. The amount of material removed is so small and the heating is so gentle that the appearance of the document is not altered.

Most ink analysis techniques rely principally on the ink dyes, but many inks contain similar dyes. For example, many black ballpoint inks contain only crystal violet, its homologues (methyl violet and tetramethyl para rosaniline), and metanil yellow. As a result, it is difficult to differentiate such inks from one another. These inks can be differentiated by DART mass spec- trometry, however, because DART spectra contain peaks from ink compo- nents other than dyes. The non-dye peaks often dominate DART ink spectra. The gentle sampling by the DART ion source volatilizes some dye, but it more readily vaporizes more volatile materials, such as vehicle, lubricant, and stabilizer components. These colorless materials allow inks with similar dye compositions to be differentiated. They also are particularly important for distinguishing pigment-containing inks. Because pigments are particulate in nature, they are not readily analyzed by any ink analysis approach, including DART mass spectrometry.

DART ionization causes little or no fragmentation of the sample molecules, so the mass spectra are dominated by intact-molecule ions, M^+, and protonated molecules, $[M+H]^+$. Each ink component therefore typically produces a single peak in the spectrum, and there is little overlap among peaks from different components. The DART source is used in combination with a time-of-flight mass spectrometer, which produces highly accurate mass determinations. Because of the minimal overlap and accurate masses, it is possible to identify many ink components unambiguously.

A library of DART ink spectra is presently being built. How well various inks can be identified from their DART mass spectra is being tested using spectrum-matching library-search software. Both commercial library software using nominal (i.e., integer) masses and non-commercial software using accurate (to 0.003 mass units) masses are being investigated. For the small number of inks analyzed so far, even the data in the nominal-mass library has been precise enough to correctly separate all but extremely similar (perhaps identical) ink formulations from one another. An ultimate goal of

the present work is the assembly of a library containing thousands of entries, which forensic scientists may then use as a reference for identifying inks found on questioned documents.

Because DART mass spectra contain peaks from vehicle components, they are sensitive to the age of the writing. This fact potentially could affect the ability to identify an ink from its DART spectrum. On the other hand, it could allow the age of writing to be estimated from its spectrum. Both of these potential consequences will be discussed.

Ink, DART Mass Spectrometry, Documents

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