J6 Characterizing Inks From Documents Using HPLC/MS

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The goal of this presentation is to provide details on how liquid chromatography-mass spectrometry may be used to differentiate individual inks of all types (i.e., ballpoint, liquid, and gel) extracted from documents.

Ink analysis within the forensic community is largely limited to imaging under a variety of lighting and filtering settings, and thin layer chromatography. Although these are often sufficient in specific cases, substantially more analytical information is available by HPLC/MS. This presentation will impact the forensic community and/or humanity by discussing the increased information and announcing the start of a library of HPLC/MS data on inks that will be available to the forensic community.

Inks are complex mixtures of dyes, pigments, resins, surfactants, and other additives in a volatile vehicle. Nevertheless, most forensic ink analysis is based principally on the dyes and pigments they contain. This ignores the additional information and the potentially greater power to distinguish one ink from another that the colorless ink components afford. Methods are under development for reliably acquiring high performance liquid chromatography-mass spectrometry (HPLC/MS) data on inks extracted from documents, with the ultimate goal of producing a library of such data so that unknown ink samples may be identified as to manufacturer and pen model by comparison with the library data. HPLC/MS data provide an inventory of both colored and colorless components and their relative abundances in a given ink, so it should be superior to thin layer chromatography in differentiating inks.

A single, 1-mm plug punched from a document is sufficient for extraction and injection onto a column for analysis. Acetonitrile works well for extracting ballpoint inks, but a mixture of dimethylformamide and water is necessary for fluid and gel inks. A C18 microbore column has provided good separation for all ink types when used with a mobile phase consisting of a mixture of water and a 50%/50% (v/v) blend of acetonitrile and methanol at a 5 IL/min flow rate. Formic acid and ammonium acetate are added as a pH stabilizer and as an ion-pairing agent, respectively. A gradient running from 30% to 90% acetonitrile/methanol is used during each run. The HPLC eluent is introduced into a single-quadrupole mass spectrometer by electrospray ionization. This interface results in little or no molecular fragmentation, so the mass spectrometer principally provides the mass of the parent molecule for each component.

Many inks contain similar dyes. For example, the only dyes many black ballpoint inks contain are crystal violet (and its byproducts, methyl violet and tetramethyl para rosaniline) and metanil yellow. Nevertheless, these inks can be differentiated by HPLC/MS both because of the differing relative amounts of crystal violet and its byproducts and because of the colorless components. Colorless components play an essential role in distinguishing pigment-containing inks. Because pigments are particulate in nature, they do not pass through the HPLC column and hence do not contribute to the HPLC/MS results. Such inks can be characterized solely by their colorless components. Resins are particularly helpful components because they generally consist of not just one molecule, but a distinctive series of species with different, equally spaced masses that elute serially from the column. A small library of data on black and blue inks is being built up as a test of the power of HPLC/MS data to differentiate ink formulas. The thirty inks tested as of this writing are all easily distinguishable from one another.

High performance liquid chromatography-Fourier transform infrared spectroscopy (HPLC/FT-IR) is another potential method for distinguishing inks. It is planned that HPLC/FT-IR will be studied. Infrared spectroscopy provides more information on the identity of a pure component than electrospray mass spectrometry does, so HPLC/FT-IR may be a useful complementary technique. A brief comparison of the two approaches will be presented.

Ink, HPLC/MS, Documents

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