A114 Analysis of Black Pen Inks by Electrospray Ionization Mass Spectrometry

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This goal of this presentation is to demonstrate a minimally destructive document sampling method with subsequent extraction and electrospray ionization mass spectrometry method for the analysis of dyes and vehicles within pen inks.

This presentation will impact the forensic community by demonstrating how sampling, extraction and analytical methods were established that caused minimal destruction to the document, extracted the ink from the paper, and detected the components within the ink. Ions from the paper did not interfere in the analysis of the ink because they could be substracted from the ink spectra. Identification of the ink components provided information for determination of ink type, i.e., ballpoint, gel, and rollerball. It also provided enough information to distinguish 16 of the 18 inks from one another, however further discrimination might be accomplished by including un - identified ions of the mass spectra.

Paper fibers containing ink samples were removed under a stereo microscope using forceps, thereby causing minimal destruction of the document. Only a few fibers were required to detect the dye components within the ink by electrospray ionization mass spectrometry. However, to detect the vehicle components, an average of thirty fibers was required since the concentrations of the vehicles within the ink are significantly lower than those of the dyes. Typically, methods of ink analysis utilize thin layer chromatography to detect the dyes and gas chromatography to detect the vehicles which are more volatile than the dyes. Electrospray ionization mass spectrometry (ESI-MS) detects both dyes and vehicles with only a couple of instrumental variations. The detection of the vehicle components is essential for the analysis of inks from gel or rollerball pens, which typically contain pigments rather than dyes. Pigments are insoluble and therefore not detectable by ESI-MS. Identification of the dyes and vehicles contained within each of ink samples provided enough information to distinguish most of the inks from one another.

Eighteen black ink pens were used in this study; six ballpoint, six gel, and six rollerball. An extraction method suitable for all types of pens was examined by varying the solvent and conditions of the extraction. Instrumental methods were investigated by varying several operating parameters such as mobile phase additive, analysis polarity (positive and negative), and applied fragmentor voltage. Mobile phase additives were required to promote ionization of some of the dye and vehicle molecules for detection in the mass spectrometer. Liquid chromatograph pumps were used to supplied mobile phase solvent; however, no chromatography was performed. The sample was introduced into the mobile phase through a standard injection loop and any necessary additives were added into the flow by a syringe pump at a point after sample introduction and before the ESI interface. Multiple injections were performed during a single analytical run including solvents blanks, a control sample of the paper with no ink, and the sample of ink extracted from the paper. This procedure facilitated quality paper background and baseline subtractions from the ink spectra. The resulting corrected spectra were dominated by ions from components in the ink. Eleven papers were examined to determine if ions from the paper interfered with the analysis of the inks. Several dye and vehicle standards were analyzed to identify some of the ink components. Estimated limits of detection of these standards were determined to evaluate the concentration of dyes and vehicles extracted and detected utilizing these methods.

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Electrospray Mass Spectrometer, Ink, Document Examination

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