J6 Development of a Web Site Database of Dyes Commonly Used in Pen Inks

Jamie D. Dunn, BS, and John Allison, PhD, Department of Chemistry, Michigan State University, East Lansing, MI; and Jay A. Siegel, PhD, Michigan State University School of Criminal Justice, East Lansing, MI*

A web site is currently under development (supported by the National Institute of Justice) that provides laser desorption mass spectrometry (LDMS) and thin-layer chromatography (TLC) data on pen inks. The web site specifically focuses on experimental data from techniques used to analyze the colorants in pen ink. The goals of this presentation are to show how to access the web site and discuss detailed information that can be obtained.

Methods: Dyes in pen inks of various manufacturers and colors are being identified using a combination of TLC, LDMS, and photodegradation. The results are being made available to the scientific community through a web site. A PerSeptive Biosystems matrix- assisted laser desorption/ionization (MALDI) time-of-flight mass spectrometer was utilized to analyze ink samples directly from paper. Samples are mounted on a modified MALDI plate. The instrument utilizes a pulsed nitrogen laser that desorbs and ionizes the dyes from the ink samples. The instrument is capable of analyzing positive and negative ions. Both ion modes were utilized for each ink sample. Several TLC solvent systems were evaluated for maximum dye separation, and the specific solvent system is posted on the web site for each pen ink sample. Several light sources were evaluated for imple- menting photodegradation of ink in order to assist in dye identification.

Results: Included on the web site are three methods of analysis that include TLC, LDMS, and photodegradation. TLC is a simple ana- lytical technique commonly used in forensic laboratories to separate dye components in pen ink and identify the color of each dye. For a given pen, the thin-layer chromatogram will be shown on the web site. LDMS has been used successfully to analyze a variety of ionic and neutral dyes or pigments used in inks, directly from paper. The web site will present positive and negative ion mass spectra of pen inks on paper. Dyes selec- tively absorb the UV laser light forming positive and/or negative ions for MS analysis. Generally, LD mass spectra only contain peaks that corre- spond to the intact dye, thus obtaining molecular weight information for the dye is easy. LDMS spectra and TLC chromatograms compliment one another, and the relationship will be established on the web site. The dyes that constitute the TLC colored bands can be specifically linked to the peaks in a LD mass spectrum. The identity of the ink dyes will be established, and be made available on the web site. Once the identities of the dyes in pen ink are known, a variety of other methods, such as high performance liquid chromatography (HPLC) or UV-Vis spectrophotometry could be implemented by forensic examiners for ana- lyzing their particular questioned document.

TLC and LDMS provide limited information (color and molecular weight of the dye, respectively). These methods alone may be insuffi- cient to determine the identity of the dye. LDMS analysis frequently requires additional experiments to characterize the dyes. Laser desorption is a desorption/ionization technique that does not induce dye fragmentation, thus limiting the information that can be obtained from the mass spectrum. The efficiency of the desorption process leads to difficulty in characterizing dyes. The authors have been developing and using photodegradation methods combined with LDMS to identify the structure of the dye.

The web site will also provide information on the variability that can be encountered in pen inks of the same brand. Generally, most blue and black ballpoint pens contain Crystal Violet as the prominent dye in the ink, but these are just a small class of pens that are used daily. In fact, pen manufacturers may use a combination of dyes and the resources for colorants are unlimited. It should also be noted that the dyes used in a specific brand of pen ink vary. Batch-to-batch dye variations have been seen to occur in BIC Round Stic® ballpoint pens with red ink. To show the variation in ink composition, six BIC Round Stic® pens were collected from random sources (increasing the variability in batch com- position), and the dye(s) in the ink of each pen were examined by LDMS. There are distinct differences in the LDMS spectra that differ- entiate among pen inks of the same brand. The spectra of the six pen inks could be generally classified into three categories.

Conclusion: The goal is to provide a searchable database that could assist investigators in making possible links between ink samples and pen types. Through the web site, one could select a dye or a mole- cular weight, and search the database to determine which pens have been found to contain these dyes.

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 ** Presenting Author*