



Questioned Documents Section – 2011

J21 Differentiation of Black Permanent Marker Inks by Ultraviolet-Visible-Near Infrared Spectrophotometry and Fourier Transform Infrared Spectrometry

Walter F. Rowe, PhD*, and Allison M. Fuchs, BS, Department of Forensic Sciences, The George Washington University, 2100 Foxhall Road Northwest, Washington, DC 20007

After attending this presentation, attendees will understand how Ultraviolet-Visible-Near Infrared Spectrophotometry (UV-VIS-NIR) and Fourier Transform Infrared Spectrometry (FTIR) may be used to differentiate brands of black permanent markers.

This presentation will impact the forensic science community by showing the high level of discrimination of different brands of black permanent marker that can be obtained through the use of UV-VIS-NIR spectrophotometry and FTIR spectrometry.

Identifying the formulation of an ink can be important for questioned document examinations. Knowledge of ink formulations can help determine the authenticity of a document, including its age and the presence of any alterations of the document. Permanent markers are commonly available and widely used writing instruments; they are used particularly for labeling items made from non-porous materials, such as glass and plastic. Ultraviolet-visible near-infrared spectrophotometry (UV-VIS-NIR) has been used to analyze ball pen and gel pen inks with some degree of success. Several studies have been conducted on the differentiation of ball pen inks using Fourier Transform Infrared (FTIR) spectrometry. The application of these two spectroscopic methods of analysis to black permanent marker inks in an effort to determine their utility for the differentiation of black permanent marker inks have been examined.

Fifteen brands of black permanent marker were purchased in Virginia, Ohio, and the District of Columbia. For brands that had more than one marker per pack, all markers in the pack were tested separately to ensure consistency within the brand. This gave a total of forty-eight markers. Scribble sheets were created with each marker using 1-inch squares of filter paper. The UV-VIS-NIR spectra of the scribble sheets were recorded in reflection mode using a UV-VIS-NIR spectrophotometer equipped with an integrating sphere. The reflectance spectra were scanned from 300 nm to 2000 nm. The infrared spectra were scanned in reflectance mode from 700 cm^{-1} to 4000 cm^{-1} using a Fourier Transform Infrared spectrometer equipped with an infrared microscope. Samples for infrared analysis were prepared by extracting ink from a 7-mm disk punched from the scribble sheets. Each disk was extracted with 40 μL of methanol; extracts were then spotted on the dull side of a clean sheet of aluminum foil and allowed to air dry. Care was taken to obtain spectra only from regions of the spotted samples where no dye separation was evident. The infrared spectra of the permanent marker inks showed the characteristic absorption features of triaryl methane dyes; in general the infrared spectra of the permanent markers were similar to those of ball pen inks.

The UV-VIS-NIR spectral data were scaled and then subjected to principal components analysis (PCA). The UV-VIS-NIR spectral range from 400 nm to 1300 nm was used for PCA to avoid fluorescence and NIR absorptions of the filter paper substrate. Only the infrared spectral range from 800 cm^{-1} to 1800 cm^{-1} of the FTIR spectra was used. The truncation of the infrared spectra was carried out to reduce the number of variables in the PCA; the spectral region selected was also observed to contain the most significant spectral variation among the permanent marker samples. The latent factors extracted by PCA were used to carry out agglomerative hierarchical clustering (AHC) and linear discriminant analysis (LDA). Based on their UV-VIS-NIR spectra the fifteen brands of black permanent markers could be placed in nine groups. UV-VIS-NIR spectrophotometry was found to have a discriminating power (DP) of 0.848. Based on their infrared spectra, the

markers could be placed in four groups. FTIR was found to have a DP of 0.714. Combining FTIR with UV-VIS-NIR spectrophotometry did not provide any additional discrimination among brands.

UV-VIS-NIR and FTIR analyses are minimally non-destructive tests and can be conducted on inks *in situ* on a substrate. While they do not provide complete discrimination of brands of permanent markers, they do provide a degree of discrimination that may be useful in many forensic investigations.

Questioned Documents, UV-VIS-NIR Spectrophotometer, FTIR