J18 Analysis of Writings Made With Black Gel Pens

Rachel Dubin, MFS, Elizabeth Hirst, BS, and Walter F. Rowe, PhD, George Washington University, Department of Forensic Sciences, 2036 H Street, Washington, DC 20052*

After attending this presentation, attendees will learn about the diffi- culties encountered in the analysis of black gel inks. They will also learn about the application of thin-layer chromatography, visible-near infrared reflectance spectrophotometry and scanning electron microscopy to the analysis of black gel inks.

This presentation will impact the forensic community showing the value of scanning electron microscopy as a tool for the analysis of black gel inks, which are difficult to characterize by more conventional means.

Forensic document examiners are frequently asked to identify the type of writing instrument that has been used to create a specific document. These examinations are conducted in cases that involve fraudulent checks, forged signatures, altered or forged documents, ransom notes and threatening letters. The advent of the gel pen complicated the work of document examiners by giving them a new type of writing implement to identify.

Gel pens were first manufactured in Japan in 1984 by Sakaura Color Products Corporation, as a "green" alternative to inks that contained volatile organic compounds. Gel inks are an environmentally friendly alternative to traditional types of ink. Multiple factors have led to the growing popularity of these pens. Gel pens are inexpensive, their writing is archival quality; they are long writing and can be purchased in almost any color.

After the introduction of the gel pen to the American market, methods were needed to allow document examiners to classify and differentiate this type of ink. Currently, there are a number of methods being used to analyze gel pen inks. These methods include visual examination with a variety of illuminants (e.g. room light, infrared and ultraviolet), thin-layer and gas chro- matography (TLC and GC), visible-near infrared reflectance spectropho- tometry, Raman scattering and scanning electron microscopy (SEM).

Mazzella and his co-workers used three techniques to determine if blue gel pens could be differentiated. Thirty-three samples were examined using filtered light examination, Raman scattering and SEM. It was determined that differentiation was possible among samples of blue gel pens, and that the blue gel writings exhibited four different morphologies when examined with the SEM. It was concluded that Raman scattering and the SEM had the highest discriminating power when examining blue gel ink.

Wilson, LaPorte, and Cantu have reported on the analysis of black gel pens using microscopy, visible and near infrared reflectance, near infrared luminescence, spot tests, thin-layer chromatography (TLC), visible-near infrared reflectance spectrophotometry and gas chromatography-mass spec- trometry. This group developed a flow-chart that differentiated black gel inks into nineteen groups. Not all brands of black gel pens could be uniquely distinguished.

In the present study, writing samples made with black gel pens were examined by a variety of techniques, including light microscopy, thin-layer chromatography, visible-near infrared reflectance spectrophotometry, x-ray fluorescence (XRF) and SEM. Writing samples for all examinations were prepared on filter paper. Ink samples for TLC were extracted from the filter paper by using methanol that was spotted on silica gel TLC plates; the TLC plates were developed with a ethyl acetate:ethanol:water (75:35:30) mobile phase. Visible-near infrared reflectance spectrophotometry and XRF were performed directly on the filter paper samples without additional sample preparation. Writing samples to be analyzed with the SEM were first sputter- coated with a 350-400 Angstrom coating of gold and palladium.

After examining all samples it was concluded that light microscopy and XRF study did not provide much differentiation of the black gel pens. One ink showed the presence of copper and another the presence of iron. This finding suggests that SEM-EDS analysis of black gel inks will not be espe- cially informative. TLC provided limited differentiation of the black gel inks: eight samples were found to contain dyes in addition to pigments; two samples showed streaking; and the colorants in nine samples did not migrate at all. This finding is consistent with the results reported by Wilson, LaPorte and Cantu. The visible-near infrared reflectance spectra of the samples from 400 nm to 1000 nm were subjected to *k* means clustering in order to identify the wavelengths that provided the greatest differentiation of the spectra. Principal component analysis (PCA) was then performed using these wavelengths. PCA identified six non-overlapping sample clusters in the reflectance spectral data. This is in contrast to the results of Wilson, LaPorte and Cantu, who identified three groups of reflectance spectra for black gel inks. An interesting correlation between the TLC results and the visible-near infrared reflectance spectra was observed: if a black gel ink showed no migration on the TLC plate, its reflectance spectrum was flat from 400 nm to 1000 nm.

From the SEM electron micrographs, the black gel inks could be placed in three main groups, based on the appearance of the gel ink on the paper fibers: smooth, smooth with particles and filamentous. Five samples were observed to have a smooth distribution of gel ink; six samples were found to have a smooth texture with a beaded appearance caused by the projection of pigment particles from the surface of the dried ink; and the remaining six samples had a filamentous appearance. Within each category, additional differences between brands of gel ink were noted. Mazzella apparently did not encounter blue gel inks with a filamentous appearance; this is a new cat-

egory that has not been previously reported. This research demonstrates the value of SEM for the examination of black gel inks.

Gel Pens, Scanning Electron Microscopy, Spectrophotometry

 ** Presenting Author*