J20 Analysis of Dry Erase Markers

Christie L. Mitchell, MFS, and Walter F. Rowe, PhD, Department of Forensic Science, George Washington University, 2036 H Street, Washington, DC 20052*

After attending this presentation, attendees of this presentation will learn about the composition of dry erase markers and about the best methods for the analysis of writings made with these writing instruments.

This presentation will impact the forensic community by highlighting problems with the application of conventional analytical methods used in questioned document examinations (such as thin-layer chromatography) to the analysis of dry erase markers. This paper will also present an analytical protocol combining visible-near infrared reflectance spectrophotometry and Fourier-transform infrared spectrometry that provides a high degree of brand differentiation.

Dry erase markers are commonly found in schools, offices, and homes but there has not been much published research on the differentiation of the brands of dry erase markers currently available. This type of research would be significant for questioned document examiners because it would enable them to determine the brand of dry erase marker that may have been used in the production of a questioned writing. In this study, nine different brands of dry erase markers were studied. Black, blue, red, and green markers were obtained for six brands and black, blue and red markers were obtained for three brands. A variety of analytical techniques were applied to the markers in an attempt to distinguish dry erase markers of the same color but distributed under different brand names. Dry erase marker were placed on filter paper "scribble sheets" and observed under a variety of illuminants (253.7 nm, 375 nm, 450 nm, 485 nm, 525 nm, and 570 nm). No fluorescence was observed for any of the dry erase markers under any of the above wave- lengths. The visible-near infrared reflectance spectra of dry erase markers on filter paper "scribble sheets" were recorded in triplicate with a UV/VIS/NIR spectrophotometer over the range of 400-1000 nm with a resolution of 1 nm. The resulting spectra were subjected first to *k* means clustering in order to identify the wavelengths of light that gave the greatest brand differentiation for each color. These wavelengths were then used to perform principle component analysis (PCA) on the reflectance spectra. Some brand differ- entiation was observed within each of the different color groups, including the black markers.

Solubility tests and thin-layer chromatography were also applied to the dry eraser markers. Such tests have been mainstays of questioned document examiners for many years. The following solvents were used in the solubility tests: petroleum ether, hexane, toluene, methylene chloride, butanol, ethyl acetate, hexafluoro-2-propanol, chloroform, ethanol, pyridine, acetone, acetonitrile, dimethylformamide, methanol, water, bleach, concentrated ammonia, 5% NaOH, 5% HCl and 5% HNO_3. Pyridine was the only solvent

in which all the dry erase marker were soluble. None of the markers were
soluble in non-polar solvents or in highly polar solvents, but were soluble to varying degrees in solvents of intermediate polarity. The variation in solu- bility in the solvents of intermediate polarity provided some differentiation between brands of the same color marker. Thin-layer chromatography was performed with both normal-phase silica gel plates and diphenyl reverse- phase silica gel plates. No significant migration or separation was observed for any of the dry erase marker samples on either type of plate. Several different mobile phases were used, including variations of the ethyl acetate
: ethanol : water (70:35:30) mobile phase on the normal-phase silica gel plates and an ethanol : phosphate buffer solution (65:35) mobile phase on the reverse-phase silica gel plates. It was determined that the colorants in dry erase markers irreversibly bind to the stationary phases of both types of plates. Therefore, the thin-layer chromatography technique is not a viable analytical technique for the analysis of dry erase markers. It was also noted that the colorants in many of the dry erase markers bind irreversibly to the cellulose fibers in filter paper. This finding suggests that cotton swabs should not be used to sample dry erase markers.

Finally, Fourier-transform infrared (FTIR) spectrometry was applied to the dry erase markers. FTIR mainly characterizes the non-colorant solids in the dry erase markers (e.g., waxes and release agents). Samples were prepared in potassium bromide disks and the infrared spectra were scanned from 4000 to 400 cm^{-1}, with a resolution of 4 cm^{-1}. Most of the infrared spectra contained a strong carbonyl peak between 1730 and 1740 cm^{-1}. This is consistent with ester functionalities in waxes. Dry erase marker samples could be grouped according to the absorptions between 1700 cm-1 and 400 cm-1. Overall, FTIR provided a similar degree of differentiation of the dry erase markers compared to visible-near infrared spectrophotometry. The two techniques can be combined to provide a higher degree of brand differenti- ation than either technique used separately. For example, visible-near infrared spectrophotometry placed the nine brands of black dry erase markers in four groups, while FTIR distinguished five groups. When the two methods of analysis were combined, the nine brands of dry erase marker were placed in seven groups.

Dry Erase Markers, Spectrophotometry, FTIR

 ** Presenting Author*