J30 Application of Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) to the Analysis of Red and Green Permanent Marker Inks

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After attending this presentation, attendees will understand the forensic potential of Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) as a method of analysis for permanent marker inks. Attendees will also understand how Principle Component Analysis (PCA), Discriminant Analysis (DA), and Hierarchical Cluster Analysis (HCA) can be used to demonstrate the discriminatory capabilities of ATR-FTIR.

This presentation will impact the forensic science community by increasing awareness of the capabilities of ATR-FTIR for the analysis of inks.

The analysis of inks serves many important functions in forensic science, including the determination of document authenticity and the comparison of document sources. The tests often require identification of the manufacturer and the specific formula of the ink. A marker is classified as a permanent marker if its ink adheres to most surfaces, has water-resistant properties, and uses dyes or pigments. Permanent markers typically contain three main components: colorants, carriers, and resins.

Numerous analytical methods have been used in the analysis of inks, and particularly of their dyes and pigments. These methods include Thin-Layer Chromatography (TLC), Liquid Chromatography (LC), Capillary Zone Electrophoresis (CZE), Infrared spectroscopy (IR), Raman spectroscopy, surface-enhanced Raman spectroscopy, Mass Spectrometry (MS), and Gas Chromatography–Mass Spectrometry (GC/MS). Various combinations of these analytical techniques may also be used.

In this study, ATR-FTIR and TLC were used for the analysis of the inks from both red and green permanent markers from eight different brands. ATR-FTIR is rapidly becoming the preferred method for acquiring infrared spectra, because little sample preparation is required: samples may simply be placed on the ATR crystal and an infrared spectrum scanned. In this instance, permanent marker inks were applied to the dull side of a sheet of aluminum foil. After the inks had dried, the inked spots on the foil were pressed against the ATR crystal. The FTIR spectra were analyzed using principal component analysis (PCA), linear discriminant analysis (DA), and agglomerative hierarchical cluster analysis (HCA). PCA is a multivariate technique that analyzes a data set in which observations are described by many inter-correlated quantitative dependent variables. Its goal is create a new, smaller set of variables that represent the meaningful variation in the original data set.

After scaling and baseline corrections, the spectra of each brand of permanent marker ink showed remarkably high consistency. Each brand had a unique infrared spectrum. For PCA, the green permanent marker inks required five components to account for more than 90% of the cumulative variance. The red permanent marker inks required six components to account for more that 90% of the variance. In DA, both red and green attained 100% correct classification for the original groupings and 100% correct classification in cross-validated groupings. TLC was performed by making “scribble” sheets on filter paper. Seven millimeter punches were taken from each “scribble” sheet. One-half of each punch was extracted into 40 µL of methanol and the extracts were spotted on silica gel TLC plates. The TLC plates were developed with a mobile phase consisting of ethyl acetate:ethanol:water (75:35:30). The developed TLC plates were examined under both normal room light and under long wavelength ultraviolet light. For each color of permanent marker, each brand of marker produced a unique chromatogram. The discriminating power of TLC and ATR-FTIR were found in this instance to be identical.

This study demonstrates that high-quality ATR-FTIR spectra of permanent marker inks can be easily obtained and that these spectra readily discriminate different brands. Further research needs to be done on alternative sampling methods, on obtaining ATR-FTIR spectra *in situ,* and on the effects of the environment on the infrared spectra of the inks.

Infrared Spectra, Ink, Chemometrics

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