



A187 Differentiation of Color Toners on Paper Using Raman Analysis and Chemometrics

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After attending this presentation, attendees will understand the advantages of using Raman spectroscopy in questioned document casework to further differentiate photocopier and laser printer toner cartridges. In addition, attendees will gain an understanding of multivariate statistics as they apply to this particular type of evidence.

This presentation will impact the forensic community by demonstrating a spectroscopic method of analysis that is not only quick and non-destructive with no sample preparation, but is not plagued by the interference of paper, also addressing the recommendations set forth in the National Academy of Sciences' report. For example, there is a need for continued research in many areas of forensic science that could contain a statistical component. In particular, visual examination and comparison of two spectra cannot always detect subtle differences. However, the same spectra could be objectively compared through the application of multivariate statistical analysis.

Toner analysis has become an area of increased interest due to the wide availability of laser printers and photocopiers. Toners contain a number of components, including, but not limited to, polymer resins, dyes/pigments, surfactants, and charge control agents. The formulation of these toners, granule size, and melting point can vary between manufactures and machines. In addition, toner is most often encountered on paper in questioned document analysis. Because of this, it is important to develop methods that limit the interference of paper without damaging or destroying the document. Previous research using Fourier Transform Infrared Spectroscopy (FTIR) has differentiated toners based on their polymer resin components. Developing a method to differentiate toners based on their other components is important for increasing the discriminating power of toner analysis.

Raman spectroscopy is a popular tool for the chemical analysis of pigmented samples. The technique involves measuring the vibrational modes of a molecule in the form of inelastic scattering of light after being subjected to a monochromatic light source, such as a laser. The use of a microscope provides a very high level of spatial resolution and depth discrimination. However, the interference from carbon black and iron oxide contained within black toner make it a problematic sample for analysis. As a result, cyan, yellow, and magenta toners were the focus for this study. Analyses were performed using a dispersive micro-Raman spectrometer equipped with a 785nm diode laser, a CCD detector, and an objective at 20X magnification. Three different methods were developed for cyan, yellow, and magenta toners on paper, respectively, to optimize results. One hundred samples of each color toner were collected. Cyan toner samples were subjected to 10% laser power with an exposure time of nine seconds for 15 scans. Yellow toner samples were subjected to 100% laser power with an exposure time of 10 seconds for 15 scans. Magenta toner samples were subjected to 25% laser power with an exposure time of 10 seconds for 30 scans. Due to the increased paper interference in the yellow and magenta toner samples, spectra of the paper for each sample were collected and spectral subtraction was performed. The data collected from these analyses was then processed using a combination of statistical procedures, including Principal Component Analysis (PCA), Agglomerative Hierarchical Clustering (AHC), and Discriminative Analysis (DA). The conclusions drawn from this study were used to form a classification scheme for each colored toner.

Raman Spectroscopy, Color Toners, Chemometrics