J17 Characterization and Discrimination of Inkjet Printer Inks Using Micro-Raman Spectroscopy

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After attending this presentation, attendees will understand the potential of micro-Raman spectroscopy to detect *in situ* chemical information from micrometric-colored spots of inkjet-printed documents from different sources.

This presentation will impact the forensic science community, with emphasis toward questioned document examiners, by exploring the chemical properties of inkjet printer inks, particularly non-extractable pigment-based samples. An example involving the counterfeiting of banknotes will be developed.

Inkjet printers are ubiquitous common devices used in various everyday activities. Due to their relative low cost and accessibility, it is not surprising that inkjet-printed documents are used for different illicit activities, including the production of counterfeited banknotes.

The printing process involves the production of a constellation of micrometric colored spots. This form of evidence makes Raman spectroscopy a suitable method for their rapid *in situ* detection, thus avoiding any extraction procedure. The Raman technique detects the phenomenon of light scattering from samples that are excited with an intense irradiation source, such as a laser. Colorants (i.e., dyes and pigments) are known to be strong Raman scatterers. While micro-Raman spectroscopy has only recently gained interest in forensic laboratories, this technique has already demonstrated its potential to be a useful method for ink analysis, especially in cases where ink extractions are not successful (i.e., pigment-based inks such as gels).

The goal of this research effort is to implement a non-destructive and relatively rapid analytical procedure for the *in situ* detection of microscopic ink spots produced by colored inkjet printers in order to help identify a (list of) printer source(s) from unknown printed specimens. For this research, the micro-Raman spectrometer is utilized to determine whether inkjet printer inks from different brands and models can be differentiated by means of their detected chemical profile. The inter-source variation of the obtained chemical profiles is studied by considering Raman data from cyan, magenta, and yellow spots. The approach consists of evaluating what colors are the most discriminating ones and if there are dependencies between these three variables, given a particular brand and model.

As a preliminary step for this project, 135 Raman spectra were captured from nine inkjet printer ink samples as well as from a counterfeited banknote, which was obtained from the collection of the Criminal Investigative Division, Treasury Obligations Section of the United States Secret Service. Extraction with methanol was carried out on all ink samples to determine if the ink was dye-based or pigment-based. Extractions were conducted on samples representing the three individual colors separately. Then, all samples were processed *in situ* on a printed document using a Near-Infrared (NIR) laser wavelength at 785nm. Cyan, magenta, and yellow spots were focused for each sample using a 50x objective lens. Five replicates per sample were obtained to verify the repeatability of the spectra. The resulting spectra were pre-processed via baseline correction, normalization, Multiplicative Scatter Correction (MSC), and Standard Normal Variate (SNV) transformation. After pre-processing, identifications of the colorants used in the ink were attempted by comparing them to a house-made reference spectral library. Data analysis of the Raman spectra was conducted using Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) in order to explore the inter-variability of the ink colors. Linear Discriminant Analysis (LDA) was carried out on the counterfeit samples to implement the structure of a system that, once a representative number of spectra is obtained, will classify the spectra with the purpose of inferring the potential brand(s) and model(s) of the inkjet printer(s) based on similar Raman profiles.

Questioned Documents, Raman Spectroscopy, Inkjet Printer