## J22 Characterization and Discrimination of Printing Inks Using DART®-MS, Py-GC/MS, and ATR-FTIR for Forensic Document Analysis

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Attendees will learn that Direct Analysis in Real Time Mass Spectrometry (DART®-MS), Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC/MS), and Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) Spectroscopy are viable methods through which inkjet inks and toners can be characterized in order to distinguish between inks and toners from different sources and associate inks and toners printed from the same source.

This presentation will impact the forensic science community by demonstrating how the combination of these three techniques provides information about the chemical profile of an ink or toner that can be used in forensic document analysis.

A total of 150 inkjet and toner samples (75 of each type) were analyzed via the three analytical methods. Each sample consisted of a monochromatic Cyan, Magenta, Yellow, and Black (CMYK) inkjet or toner printed or manually deposited onto Whatman® 42 paper. It was determined there is no significant difference in chemical profiles obtained between printed and manually deposited inkjets or toners on paper.

For ATR-FTIR, analysis was performed using a Perkin® Elmer® Spectrum One FTIR with Pike Technologies GladiATR™ Diamond Single Bounce Crystal accessory with imaging capabilities. Samples were analyzed directly on paper without destruction. Samples could be analyzed in under a minute each. Based on the chemical information obtained for toners, the 75 samples were divided into 12 different groups based on polymer content observed in the IR spectra. Toners could be easily separated into groups based on the presence or lack thereof of polystyrene, acrylate, epoxy, and polyethylene resins. However, no chemical information was obtained for inkjet samples due to strong paper background contribution.

For Py-GC/MS, an Agilent Technologies® 7890A GC with 5975 inert XL MSD, and CDS Analytical 1500 series pyroprobe were used for analysis. Toner samples were transferred to aluminum foil for analysis to remove interference of paper background at high temperature. The chemical information obtained for toners included different resins present such as toluene, styrene, substituted benzene, and naphthalene that allow for classification. Inkjets were analyzed at a lower pyrolysis temperature to desorb volatile components from the inks on paper. This method does destroy a 1x10mm cut of ink on paper. For inkjets, volatile organic compounds such as diols, pyrrolidinone, glycols, and glycerols were observed that make up the chemical profile.

For DART®-MS, analysis was performed using an Agilent 6530 Q-TOF mass spectrometer and IonSense DART®-SVP. Both toner and inkjet samples were analyzed directly on paper with no sample preparation or destruction. A spectrum for each sample could be produced in less than two minutes. The mass spectra for inkjets include Polyethylene Glycol (PEG) mass fragments with differences of 44 Da that are characteristic for each sample. Toner samples also produce characteristic spectra with polymer-like distributions that are significantly different from the paper background.

Overall, the combination of these techniques and the fusion of the data provides comprehensive information to distinguish between inks and toners printed from different sources and associate inks and toners printed from the same source without requiring extensive sample preparation or total destruction to a document.

**Inkjets, Toners, Spectrometry**

 ** Presenting Author*