B155 Analysis of Inks Via a Microfluidics Extraction Device With a Quadrupole Time-of-Flight Mass Spectrometer (qTOF/MS)

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After attending this presentation, attendees will better understand a new Microfluidics Device (MFD) that can facilitate extraction of dyes, inks, etc. as well as a new understanding of analyzing inks from questioned documents via tandem mass spectrometry. Originally, the MFD was used for the extraction of dyes from fibers with minimal room for error because of the lack of contact between the examiner and the evidence.[1] Proven as a useful tool in previous work, the use of the MFD has expanded to analgesic tablet analysis and now to ink analysis from questioned documents, the main focus of this presentation.

This presentation will impact the forensic science community by providing a fast, accurate, and reproducible extraction and analysis methodology for a variety of evidences with minimal areas for human error and minimal damage to the evidence. For MFD Mass Spectrometric (MS) analysis, only a small amount of the evidence is needed, whether it is a single fiber a couple millimeters in length from a piece of fabric or a small microchip of the questioned document. This ensures that the majority of the evidence is preserved for court proceedings.

In these experiments, a variety of pens, markers, and highlighters in colors such as red, orange, yellow, and pink were analyzed using MFD-MS via Agilent® Technologies' 6520 quadrupole Time-of-Flight (qTOF). From previous work, it is known that Rhodamine 6G (Rh6G) and Rhodamine B (RhB) are common dyes found in writing utensils of these colors.[2,3] Both of these compounds were purchased from Sigma Aldrich® and used as standards for reference. The six writing utensils analyzed were obtained from a variety of manufacturers such as Sharpie® and Office Depot®. All experiments were completed at North Carolina State University in the analytical chemistry laboratory of the College of Textiles in Raleigh, NC.

Sample preparation consisted of drawing a single line to represent writing on a questioned document. A Harris Micro-Punch tool with a 2.0mm hole was used to take a micro-punch of the document. Due to markers having a larger amount of dispensed ink than pens such as ball point pens, only about a third of the micro-punch taken contained ink to ensure that saturation of the mass spectrometer detector would not occur, which indicates that more of the writing is preserved on the document. The micro-punch was then placed in the sample chip and inserted into the MFD. The extraction proceeded within the MFD using the program created in-house.[1] Acetonitrile (ACN) was flushed into the chamber of the cavity containing the micro-punch to extract the ink from the paper. This was done four times to ensure that extraction had occurred. Mass spectra were obtained via the qTOF mass spectrometer. The exact mass was identical for both Rh6G and RhB (443.2329); however, their structures differed and could be differentiated by their fragments when targeted via Tandem MS (MS/MS). RhB fragmentation included the loss of -CO2 which was observed by a fragment ion with m/z of 399; Rh6G fragmentation included the loss of -C2H4 which was observed by a fragment ion of m/z of 415.[3] This identification can be used to determine if one or both rhodamines are in the extracted ink. After each sample was analyzed, the MFD/MS system was flushed with Isopropyl Alcohol (IPA) until the ions of interest were low in abundance, and a blank sample was recorded to ensure that signals observed with the samples were from the extracted dyes. Total analysis and cleaning time per sample was estimated to be approximately 15-20 minutes depending on the user's knowledge of the system.

In conclusion, this analysis system in conjunction with the use of Rh6G and RhB as standards for red, orange, yellow, and pink writing utensils provides a new methodology to analyze questioned documents. Determination of whether the markers contained the rhodamines and, if so, which ones, have been successful and through repetition have shown that this technique is accurate and reproducible. Analysis time is decreased exponentially and minimal damage is done to the questioned document, ensuring that the majority of the evidence is conserved for later use.

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Reference(s):

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Ink Analysis, Mass Spectrometry, Microfluidics