J11 Direct Sample Analysis/Mass Spectrometry (DSA/MS) vs. Separation MS Techniques for the Analysis of Writing Inks

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After attending this presentation, attendees will better understand DSA/MS of writing inks and its comparison to Liquid Chromatography/Mass Spectrometry (LC/MS) and Gas Chromatography/Mass Spectrometry (GC/MS) of the same inks.

This presentation will impact the forensic science community by introducing a new method for the analysis of writing inks and the advantages and disadvantages compared to GC/MS and LC/MS.

Official documents are an essential aspect of almost all legal agreements. Such widespread use of documentation also comes with a large amount of forgery. Criminal acts may include the altering or addition of entries to change the value of the document. Questioned document examinations are therefore required to determine the presence of unoriginal writing within the document. Direct Sample Analysis (DSA) coupled with high resolution, high mass accuracy Time-Of-Flight Mass Spectrometry (TOF/MS) is an emerging technique for the in situ analysis of various substances. DSA is similar to Desorption Electrospray Ionization (DESI) and Direct Analysis in Real Time (DART); however, it uses an atmospheric pressure chemical ionization source for ionization of organic compounds. In this study, DSA was applied to the identification of 80 black and blue writing inks from both ballpoint and non-ballpoint pens. Moreover, the results obtained from DSA analysis were compared with the extraction of the ink from the paper and its analysis by Gas Chromatography/Mass Spectrometry (GC/MS) and nano ultra-high performance Liquid Chromatography-Orbitrap Mass Spectrometry (nLC/MS).

Eighty ink samples were obtained from the United States Secret Service. Approximately 3mm sections of each writing were placed on the DSA sample holder and analyzed in an automated fashion. The holder can analyze 13 samples in a serial manner. Utilizing a high mass accuracy TOF/MS and using internal calibration, mass accuracy of <6 ppm was achieved. DSA analysis was performed on a Perkin Elmer AxION DSA in conjunction with a Perkin Elmer AxION 2 Time-Of-Flight Mass Spectrometer operating at a resolution of ~10,000 at m/z 922. For HPLC analysis, a Thermo Fisher Scientific Easy-nLC 1000 Ultra High Performance Liquid Chromatograph was used in conjunction with a Thermo Fisher Scientific Velos Pro Orbitrap Elite Mass Spectrometer. Two different LC methods were developed one with the analysis time of 30 minutes and the other with the analysis time of 5 minutes. GC/MS analysis was performed on a Perkin Elmer Clarus 680 Gas Chromatograph-Clarus SQ 8C Mass Spectrometer using electron ionization.

Analysis by DSA and LC/MS resulted in the identification of colorants as well as vehicles and additives while analysis by GC/MS mainly resulted in the identification of the non-colorant ingredients. DSA-high resolution MS, as well as Liquid Chromatograph Orbitrap Mass Spectrometry (LC-Orbitrap/MS), provided extensive compositional information. DSA detected more ink related compounds and in more samples than LC/MS. Of the three techniques utilized, DSA provided the greatest number of ink compound identifications and in more samples. Both DSA and LC/MS were able to detect colorants; however, the DSA results were obtained within seconds of mounting the sample while LC/MS analysis took several minutes. In addition to longer analysis time, solubility issues and the elution of small highly charged compounds with the void volume were other main draw backs of LC/MS.

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Under LC/MS; however, salts are separated from compounds of interest and most compounds are separated from each other, minimizing the suppression effects and simplifying compound identification. In regards to sample preparation, neither method showed a significant advantage over the other. Although LC/MS required an additional extraction step, mounting and aligning samples in the DSA was tedious. Currently, a disadvantage of the DSA method is that samples must be cut out of a document and carefully positioned on the sample stage to be analyzed. GC/MS and LC/MS are indeed informative techniques, but they are also destructive methods, unlike spectroscopic methods such as Attentuated Total Reflectance/Fourier Transform Infrared (ATR-FTIR) and Surface-Enhanced Raman Spectroscopy (SERS); however, the spectroscopic techniques are less informative. GC/MS was shown to be the least informative analysis method for ink compositions, since colorants were mostly not detected and solvents and volatile components detected by GC/MS tend to disappear very rapidly. For profiling purposes, the use of multiple methods, such as the combination of DSA, LC/MS, and GC/MS as shown in this study, is necessary because no single method detects all components in ink formulations.

Direct Sample Analysis TOF/MS, Nano UHPLC/MS, Ink Chemical Composition

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