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Technical Note

A comparison between DART-MS and DSA-MS in the forensic analysis of writing inks

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ABSTRACT

Ambient ionization mass spectrometry is gaining momentum in forensic science laboratories because of its high speed of analysis, minimal sample preparation, and information-rich results. One such application of ambient ionization methodology includes the analysis of writing inks from questioned documents where colorants of interest may not be soluble in common solvents, rendering thin layer chromatography (TLC) and separation–mass spectrometry methods such as LC/MS (-MS) impractical. Ambient ionization mass spectrometry uses a variety of ionization techniques such as penning ionization in Direct Analysis in Real Time (DART), and atmospheric pressure chemical ionization in Direct Sample Analysis (DSA), and electrospray ionization in Desorption Electrospray Ionization (DESI). In this manuscript, two of the commonly used ambient ionization techniques are compared: Perkin Elmer DSA-MS and IonSense DART in conjunction with a JEOL AccuTOF MS. Both technologies were equally successful in analyzing writing inks and produced similar spectra. DSA-MS produced less background signal likely because of its closed source configuration; however, the open source configuration of DART-MS provided more flexibility for sample positioning for optimum sensitivity and thereby allowing smaller piece of paper containing writing ink to be analyzed. Under these conditions, the minimum sample required for DART-MS was 1 mm strokes of ink on paper, whereas DSA-MS required a minimum of 3 mm. Moreover, both techniques showed comparable repeatability. Evaluation of the analytical figures of merit, including sensitivity, linear dynamic range, and repeatability, for DSA-MS and DART-MS analysis is provided. To the forensic context of the technique, DART-MS was applied to the analysis of United States Secret Service ink samples directly on a sampling mesh, and the results were compared with DSA-MS of the same inks on paper. Unlike analysis using separation mass spectrometry, which requires sample preparation, both DART-MS and DSA-MS successfully analyzed writing inks with minimal sample preparation.

1. Introduction

Forensic science focuses on the application of science to the law, and has many sub-disciplines, including questioned document examination. Questioned document examination includes a thorough characterization of the composition of inks used in questioned documents, such as forged checks or business contracts [1–3]. Questioned document examiners may be able to determine, based on the ink, what type of pen was used; if more than one ink is present on the same document; the potential age of the ink; and the geographical distribution of the ink (i.e., where the ink is produced), to trace the original document back to a potential location [2]. Inks have different chemical compositions based on the type of writing instrument used. Several types of writing instruments include ballpoint pens, gel pens, fountain pens, and felt-tip pens or "markers" [4]. Moreover, multiple inks with the same color may be present on the same document; however, they can be differentiated by their chemical composition (profiles) [3].

Inks are a complex mixture consisting of a liquid vehicle, which is the liquid portion of the ink which transports colorants onto a surface; a colorant (a dye or a pigment); and additives [5–7]. Colorants impart color to the ink, and may include dyes or pigments such as carbon black, Michler's ketone, crystal violet, or their combinations. Dyes are soluble within the vehicle whereas pigments are insoluble, solid, ground-up material suspended in the vehicle. Whether a colorant is a dye or a pigment depends upon the vehicle, and therefore, the type of ink. Lastly, additives include a wide variety of materials, including *pH* modifiers, emulsifiers, and

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buffers [8]. Pigments, being insoluble in the vehicle, may be insoluble in common solvents used in gas or liquid chromatography mass spectrometry (GC–MS or LC–MS) or electrospray-based mass spectrometry (ESI-MS), limiting the information which can be obtained.

Ambient ionization techniques are becoming increasingly popular in laboratories due to their short analysis time and minimal sample preparation enabling high throughput analysis. Ambient ionization mass spectrometry uses a variety of ionization techniques such as penning ionization in Direct Analysis in Real Time (DART), and atmospheric pressure chemical ionization in Direct Sample Analysis (DSA), and electrospray ionization in Desorption Electrospray Ionization (DESI). While the scope of DSA-MS in forensic casework is limited, DSA-MS has been used in forensic drug analysis for the examination of phenethylamines, and in ink analysis [6]. On the other hand, DART-MS has been extensively used for the analysis of explosives, paints, gunshot residue, and drug analysis [9–13]. Current DESI-MS techniques are only capable of detecting dyes and additives in questioned documents [6,14]. Current techniques of ink analysis in questioned document cases also include LC/MS(-MS), GC/MS, and MALDI-MS [15–17]. Recently, we compared analysis of writing inks using DSA-MS, GC–MS, and LC–MS. Briefly, 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 detectable by GC–MS tend to disappear very rapidly. Both DSA-MS and LC–MS were able to detect colorants; however, the DSA-MS 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, and longer sample preparation time were other main drawbacks of LC–MS. DSA-MS detected more ink-related compounds and in more samples than LC–MS. In this article, we compare DSA-MS with another commonly used ambient ionization technique, DART-MS.

DART-MS and DSA-MS techniques are ideal for the analysis of ink since ink samples can be introduced into the ionization region using the same medium that they are dispersed in. DSA-MS is an ambient ionization technique that utilizes atmospheric pressure chemical ionization (APCI) in which heated nitrogen gas is ionized by an electrical discharge, which initiates the desorption and ionization process [18]. Nitrogen ions ionize water molecules in the source and form water cluster ions that will ultimately ionize the analytes of interest. DSA-MS utilizes a closed system in which samples are introduced via a sample holder containing 13 sampling spots inside a closed housing. The housing is continuously swept with the flow of nitrogen gas from the APCI source that minimizes the ambient air entering the housing, thereby reducing chemical background noise. DART-MS on the other hand uses a penning ionization technique to initiate the ionization process, relying upon the formation of metastable helium atoms to generate protonated water clusters, which then ionize the analyte of interest [6,19]. DART-MS uses an open source in which individual samples on a variety of media are introduced into the ionization region as individual samples or placed on sampling trains for automated analysis. Both DSA-MS and DART-MS can be used to analyze ink samples taken directly from questioned documents. The purpose of this Technical Note is to report an evaluation of the analytical figures of merit including sensitivity, linear dynamic range, and repeatability, for DSA-MS and DART-MS analysis of writing inks, with specific regard to the analysis of colorants, and demonstrate the application of DART-MS to the analysis of United States Secret Service ink samples directly on a sampling mesh.

2. Materials and methods

2.1. Sample preparation

Details on the methodology for analyzing writing inks for DSA-MS and DART-MS have been previously published [6–8]. To compare the performance of the two techniques for the analysis of writing inks, three pens were used: a Paper Mate Stick blue ballpoint pen, a Bic Atlantis blue ballpoint pen, and a Zebra black gel pen. These were unaged ink samples. To use an identical sample introduction, the DSA-MS sample mesh holder was used. The DSA-MS mesh holder directly fits on the DSA-MS system. To use the same mesh holder on DART-MS, a sampling train was fabricated in house (Fig. 1). All mesh screens were burned prior to analyzing ink samples.

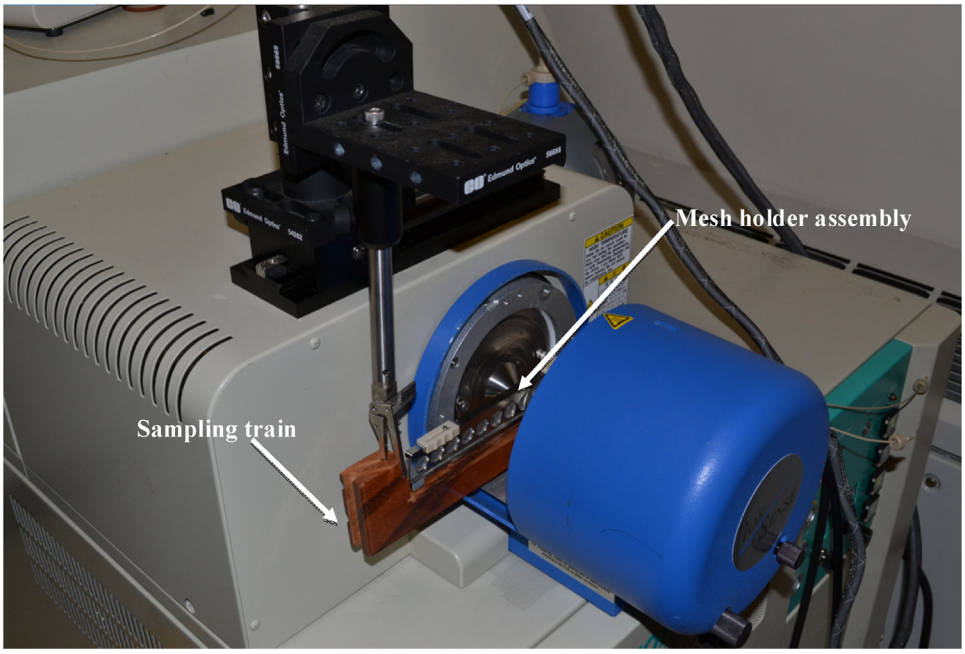

Fig. 1. In-house fabricated sampling train.