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Trace analysis of energetic materials via direct analyte-probed nanoextraction coupled to direct analysis in real time mass spectrometry☆

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ABSTRACT

Direct analysis in real time mass spectrometry (DART-MS) has proven to be a useful forensic tool for the trace analysis of energetic materials. While other techniques for detecting trace amounts of explosives involve extraction, derivatization, solvent exchange, or sample clean-up, DART-MS requires none of these. Typical DART-MS analyses directly from a solid sample or from a swab have been quite successful; however, these methods may not always be an optimal sampling technique in a forensic setting. For example, if the sample were only located in an area which included a latent fingerprint of interest, direct DART-MS analysis or the use of a swab would almost certainly destroy the print. To avoid ruining such potentially invaluable evidence, another method has been developed which will leave the fingerprint virtually untouched. Direct analyte-probed nanoextraction coupled to nanospray ionization-mass spectrometry (DAPNe–NSI-MS) has demonstrated excellent sensitivity and repeatability in forensic analyses of trace amounts of illicit drugs from various types of surfaces. This technique employs a nanomanipulator in conjunction with bright-field microscopy to extract single particles from a surface of interest and has provided a limit of detection of 300 attograms for caffeine. Combining DAPNe with DART-MS provides another level of flexibility in forensic analysis, and has proven to be a sufficient detection method for trinitrotoluene (TNT), RDX, and 1-methylaminoanthraquinone (MAAQ).

1. Introduction

As the use of improvised explosive devices (IEDs) grows, so does the need for a method to detect the materials used in the manufacturing process. As such, the rapid detection of ultra-trace explosives and related compounds is of the utmost importance to forensic investigators. Perhaps even more important, however, is the need to link these devices to a manufacturer. There is occasion for such a link in the event of explosive residue within a latent print left on a detonator or other surfaces at the scene. Detecting explosive residues without destroying the latent fingerprint would be the most ideal outcome, providing information regarding both the substance and potential person of interest.

Many methods capable of direct sampling have been developed for trace analysis of energetic materials. Ion mobility spectrometry is perhaps the most commonly used for this application in field analyses [1]. Numerous other instrumental approaches have also emerged for field and laboratory use, including Raman spectroscopy; chemical, electrochemical, and luminescence sensors; and mass spectrometry [2]. Interest in ambient ionization mass spectrometry techniques has grown from the desire for direct sample analysis and divergence from thermal desorption/gas phase ionization. Many such methods, most notably direct analysis in real time mass spectrometry (DART-MS) [2–5] and desorption electrospray ionization-mass spectrometry (DESI-MS) [6], have been successfully used for analyses of trace explosives and have the advantages of rapid analysis and reduced sample preparation [7]. However, they all trade specificity for high-throughput [8], increasing spectral noise due to matrix effects and thereby decreasing analyte signal intensity.

Additionally, techniques capable of analysis of explosive residues within a latent fingerprint often destroy the print – DESI-MS

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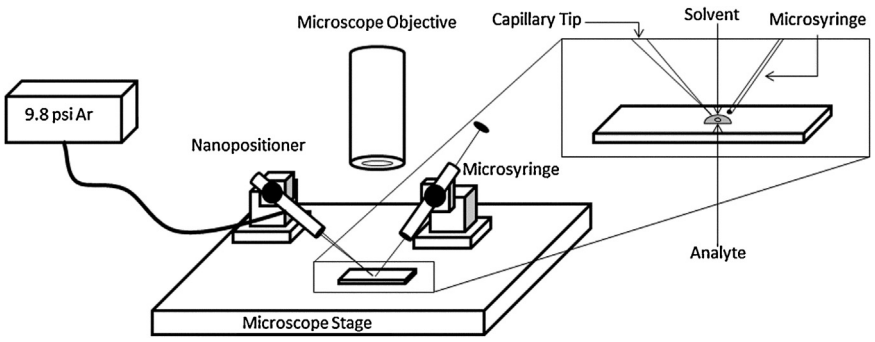

Fig. 1. Schematic of an extraction with the nanomanipulator. The enlarged area shows the analyte particle in the solvent injected by the microsyringe.

essentially electrosprays solvent onto a surface to facilitate desorption creating several aberrations in the print [9], and most sample recovery techniques (e.g., washes or swabs) would inherently smear or remove the print. DART-MS is an atmospheric ionization technique that may be performed either directly from the surface on which the sample is found [3] (within reasonable spatial considerations) or from a probe on which the sample has been deposited [4]. Using a helium or nitrogen glow discharge, analytes (generally below 1000 Da) placed in the beam are ionized via mechanisms previously described by Cody et al. [10] and Song et al. [11,12].

DART-MS has shown success in forensic analyses of pharmaceuticals [13–15], biological samples [16,17], illicit drugs [18–25], chemical warfare agents [26], inks [27], and explosives [2–5]. Analyses of organic explosives directly from many surfaces including glass, asphalt shingle, polyurethane foam, wood and metal have typically yielded clean spectra [3]. However, lipids and inorganic salts are common components of latent fingerprints [28] and are easily detected via DART-MS [29]. This often creates complex spectra when determining trace analytes in latent prints; also, some analytes are either not detected or detected at very low intensities [4]. Therefore, a new method or alteration of current methods is desired to obtain both accurate trace analyses of explosives as well as maintenance of evidence.

Direct analyte-probed nanoextraction (DAPNe) manages to alleviate the primary issues that arise with other sampling methods, including matrix effects and sample destruction [30–32]. Traditionally coupled to nanospray ionization-mass spectrometry (NSI-MS), this technique has displayed its value in trace analysis with extraction of illicit drugs from fibers [30], electrostatic lifts [31], and within fingerprints [32]. Using a nanomanipulator mounted to the stage of a bright-field microscope, a capillary tip with a conductive coating can be directed to a particle of interest with 5 nm translational resolution [30]. As such, DAPNe–NSI-MS can mitigate the aforementioned specificity issues seen with other ambient techniques. Additionally, this method is minimally invasive and leaves latent fingerprints virtually unperturbed, allowing the prints to be preserved for identification purposes [32]. However, NSI-MS is not a common installment in forensic laboratories.

DART-MS, on the other hand, has become quite popular in forensic mass spectrometry research in recent years [2–5,14–27]. In this study, DAPNe is coupled to DART-MS to diminish the specificity concerns of this popular technique. With this pairing, explosives can be extracted from within latent fingerprints using DAPNe and analyzed directly via DART-MS.

Trinitrotoluene (TNT) and RDX (cyclonite, hexogen) are commonly used organic explosives. The dye 1-methylaminoanthraquinone (MAAQ, Disperse Red 9) is commonly combined with explosives and position-sensitive sensors in dye packs designed to mark the unauthorized removal of currency from a secure location [33]. All three substances were extracted from glass slides and/or metal. MAAQ was also extracted from within fingerprints on a glass slide. All extractions were subsequently analyzed via DAPNe–DART-MS.

2. Experimental

Methanol, acetone, and MAAQ were obtained from Sigma–Aldrich Co. (St. Louis, MO). TNT and RDX were obtained from AccuStandard (New Haven, CT) as 1 mg/mL solutions in methanol. Extractions were performed with a 2-positioner nanomanipulator (DCG Labs, Richardson, TX) mounted on the stage of an Olympus BX40 bright field microscope (Olympus, Center Valley, PA). A joystick controller is employed to maneuver the positioners.

In contrast to DAPNe–NSI-MS [10–12], which utilized 1 μm i.d. Au/Pd-coated nanospray tips, extractions were performed using 4 μm i.d. uncoated capillary tips (New Objective, Woburn, MA). Aspiration of dissolved analytes into the capillary tip was facilitated by a PE2000b 4-channel pressure injector (MicroData Instruments Inc., S. Plainfield, NJ). A ~1 μg/μL drop of sample solution was deposited on the surface of interest. Prior to analysis, the solvent was evaporated, and the crystals formed on glass slides or metal. For extractions from within a fingerprint, a finger was slid over the analyte spot and then used to place a fingerprint on a second glass slide.

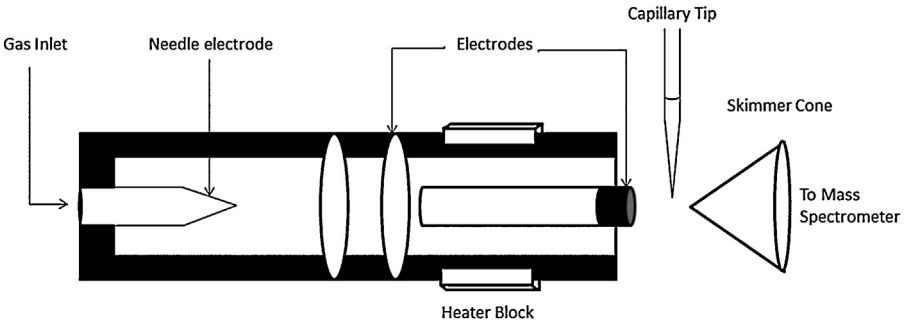

Fig. 2. Schematic of the DART ionization source with the capillary tip post-extraction.