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Technical note

A method for rapid sampling and characterization of smokeless powder using sorbent-coated wire mesh and direct analysis in real time - mass spectrometry (DART-MS)

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ABSTRACT

Improvised explosive devices (IEDs) are often used by terrorists and criminals to create public panic and destruction, necessitating rapid investigative information. However, backlogs in many forensic laboratories resulting in part from time-consuming GC-MS and LC-MS techniques prevent prompt analytical information. Direct analysis in real time - mass spectrometry (DART-MS) is a promising analytical technique that can address this challenge in the forensic science community by permitting rapid trace analysis of energetic materials. Therefore, we have designed a qualitative analytical approach that utilizes novel sorbent-coated wire mesh and dynamic headspace concentration to permit the generation of information rich chemical attribute signatures (CAS) for trace energetic materials in smokeless powder with DART-MS. Sorbent-coated wire mesh improves the overall efficiency of capturing trace energetic materials in comparison to swabbing or vacuuming. Hodgdon Lil' Gun smokeless powder was used to optimize the dynamic headspace parameters. This method was compared to traditional GC-MS methods and validated using the NIST RM 8107 smokeless powder reference standard. Additives and energetic materials, notably nitroglycerin, were rapidly and efficiently captured by the Carbopack X wire mesh, followed by detection and identification using DART-MS. This approach has demonstrated the capability of generating comparable results with significantly reduced analysis time in comparison to GC-MS. All targeted components that can be detected by GC-MS were detected by DART-MS in less than a minute. Furthermore, DART-MS offers the advantage of detecting targeted analytes that are not amenable to GC-MS. The speed and efficiency associated with both the sample collection technique and DART-MS demonstrate an attractive and viable potential alternative to conventional techniques.

1. Introduction

Improvised explosive devices (IEDs) are charged devices often used by terrorists and criminals to create public panic and destruction. When a bombing incident is an act of terrorism, the target of the IEDs is usually larger than the physical location of the explosion since the goal is often to instill fear and panic among the general population [1]. Methods that can provide investigators and law enforcement personnel with prompt investigative information are needed in order to prevent further acts of terrorism. Investigative information, however, is not provided quickly, in part because of time-consuming techniques employed by many forensic laboratories. As a result, the analysis turnaround time is longer, resulting in a need for instrumentation that can rapidly detect and identify the energetic materials used in the creation of these devices. Identifying the starting materials is critical as it may provide the possibility of identifying or at minimum, linking the device to the fabricator [1,2].

The fabricator of an IED will often design the device to utilize materials that are readily available. These may include common household items that contain energetic materials (ammonia- or peroxide-based materials), components of ammunition, fertilizers, etc. IEDs, however, are often constructed using black powder or smokeless powder [2]. Smokeless powder is a propellant commonly used in civilian and military ammunition and therefore readily available and easily accessible. Smokeless powder was purposefully chosen for this study because of its availability and accessibility as well as its common use for IEDs. These powders contain various additives such as plasticizers, stabilizers, flash suppressants and others that manufacturers use to partly control their burn rate in addition to their shelf life. The primary energetic materials used in most smokeless powders are nitrocellulose and nitroglycerin [1,3]. However, trinitrotoluene (TNT), nitroguanidine, and other

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nitro-organic compounds alike can also be found, but these powders are often more difficult to obtain. Different manufacturers will utilize different additive and energetic materials or the same materials in differing amounts to achieve specific performance characteristics, thus creating a unique set of identifiers that can be used as chemical attribute signatures (CAS) for a particular powder [1–3].

Current approaches to the investigation of post-blast scenes involving IEDs entail recovering fragments of the original device, post-blast residues and any partially consumed or unconsumed energetic materials used to charge the device. The two primary methods for the collection of trace explosive residues during a scene investigation are vacuuming and swabbing [4]. Trace explosive materials on a surface may be missed or may not adhere to the collection surface when swabbing and vacuuming are utilized. This can result in the collection of contaminants and extraneous materials that may overwhelm the detector's response when these samples are analyzed [5]. Furthermore, additional sample clean-up steps may be required, which will further increase the sample preparation time. Conversely, generating and concentrating headspace vapors onto an adsorbent, rather than swabbing or vacuuming, can often increase the detection sensitivity of targeted compounds [5]. Headspace vapors can be generated either using static or dynamic headspace methods. Static headspace methods, such as solid-phase microextraction (SPME), typically employ adsorption traps that are inserted into the headspace of the sample vessel to separate the targeted compounds from the remainder of the headspace gas [6]. Conversely, dynamic headspace is a purge and trap technique that uses a continuous flow of inert gas or a vacuum to constantly flush the headspace vapors through an adsorption trap, resulting in a faster and more sensitive method when compared to static headspace methods [6]. Recently, SPME coupled to ion mobility spectrometry (IMS) and GC has been employed for the collection and concentration of trace explosives and their volatile chemical signatures [5,7], including those from smokeless powder [8]. However, SPME can be a time-consuming process. As a result, dynamic headspace methods are more preferable for rapid sample preparation.

Sample collection is followed by laboratory examination and analysis of the recovered materials using presumptive and confirmatory tests in an effort to identify the materials used to charge the device. Much of the confirmatory analyses for smokeless powder and other explosive-related materials are presently conducted by fourier transform infrared spectroscopy (FTIR) [9], scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDS) [10], gas chromatography – mass spectrometry (GC-MS) [11] and liquid chromatography – mass spectrometry (LC-MS) [12]. These techniques can be, and often times are, time-consuming analytical techniques. As a result, the ability to rapidly collect, identify and characterize smokeless powders is of great forensic value.

A useful analytical approach for the forensic analysis of explosives must be able to rapidly detect the explosive components with minimal sample preparation. Furthermore, the sensitivity must be comparable or exceed that of current techniques. One such technique is DART-MS, which is capable of providing analytical results in seconds with minimal sample preparation. Furthermore, it is a minimally destructive technique, which is critical in cases where sample quantity is limited. The detection of various explosives, including nitro-organic explosives, such as those found in smokeless powder has been shown to be possible by DART-MS [13–16].

A rapid, qualitative method for the field collection and preparation of trace explosive materials utilizing sorbent-coated wire mesh consumables and portable samplers for subsequent analysis by DART-MS was designed and developed. Paint cans with lids retrofitted with Swagelok fittings were utilized to permit concentration of the smokeless powder headspace vapors onto sorbent-coated wire mesh using dynamic headspace concentration. The use of the novel sorbent-coated wire mesh technology for smokeless powder sampling aims to provide broader coverage of the additives used to formulate smokeless powder and to generate information rich CAS using DART-MS for the classification of smokeless powder. This work aims to address a relevant need of the Forensic Science community, which is to accelerate the speed of collection and analysis for explosive-related case samples.

2. Materials and methods

2.1. Materials

Hodgdon Lil' Gun (HLG) smokeless powder was obtained from a local sporting goods store as a 1 lb (454 g) canister. The National Institute of Standards and Technology (NIST) RM 8107 reference standard was obtained from the NIST Standard Reference Materials Catalog.

Samples were prepared for headspace analysis using 16 oz. aluminum paint cans with lids purchased from Fisher Scientific (Agawam, MA, USA). The lids were configured with two ports to fit two Swagelok tube fittings obtained from Cambridge Valve & Fitting Inc. (Billerica, MA, USA): a 1/4" straight thread male tube adapter (No. SS-4-TA-1-OR) and a 1/4" straight thread male O-seal connector (No. SS-400-1-OR). The stainless steel, self-sealing hex nuts (No. 91339A160) used to seal the fittings were purchased from McMaster-Carr (Robbinsville, NJ, USA). Dynamic headspace concentration was performed using a heating mantle (115 V, No. 100B CH093) with a PowrTrol Voltage Control temperature controller (No. 104A PL120) purchased from Glas-Col (Terre Haute, IN, USA). The Leland Legacy vacuum pump with the cassette holder accessory, SureSeal opaque white polypropylene cassettes (2-piece, 37 mm) and fiber glass filters (1 μm, 37 mm, type AE) were purchased from SKC Inc. (Eighty Four, PA, USA). Wire mesh was obtained from Sigma Aldrich (St. Louis, MO, USA) and coated with Carbopack X (graphitized carbon) by Supelco (Bellefonte, PA, USA). Samples and standards for GC-MS analysis were prepared in GC Resolv acetone purchased from Fisher Scientific.

2.2. Dynamic headspace concentration setup

The rationale for the design of this method is based on the E1413-13 standard issued by the American Society for Testing and Materials (ASTM) International for the separation and concentration of ignitable liquid residues from fire debris samples by dynamic headspace concentration [17]. This method is designed to prepare extracts from fire debris for GC-MS analysis. It is a standard practice for recovering volatiles from low concentrations of ignitable liquid residues using headspace concentration. Both positive and negative pressure systems are described. A positive system employs an inert gas, such as nitrogen, to purge the headspace vapors through an adsorbent tube whereas a negative system uses a vacuum to evacuate the headspace vapors out of the container. In order to demonstrate a field-portable sampling method, a negative pressure system was employed to prepare the samples for DART analysis. Negative pressure systems reduce the need for gas tanks or generators as they only require a vacuum pump. A small, hand-held vacuum pump was employed to show the portability of this sampling apparatus.

HLG smokeless powder was chosen to optimize the dynamic headspace concentration parameters because it contains a wide range of additives that are commonly found in smokeless powder. HLG (5 mg) was weighed in an aluminum dish and subsequently placed into a 16 oz. paint can sealed with a modified lid. One SKC Type AE fiber glass filter was placed into a SKC SureSeal opaque white polypropylene cassette, which was subsequently connected to one of the Swagelok fittings on the lid with a 1/4" ID Tygon tube. This served as a filter for incoming room air. Carbopack X was chosen for its proven affinity for a variety of volatile organic compounds (VOCs) and greater capture efficiency in comparison to Tenax TA [18,19]. The Carbopack X-coated wire mesh was cut into thin strips, approximately 0.75 in. in width and 1.06 in. in length so that they could be placed in the SKC white polypropylene cassettes. These cassettes were connected to the second