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Forensic analysis of a single particle of partially burnt gunpowder by solid phase micro-extraction–gas chromatography-nitrogen phosphorus detector

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ABSTRACT

Solid phase micro-extraction (SPME) was adopted to extract organic gun shot residues (OGSRs) from a single particle of partially burnt gunpowder. The partially burnt particle samples were collected from gun shot residue (GSR) deposited near the target areas. OGSRs, such as diphenylamine (DPA), methyl centralite (MC), ethyl centralite (EC), from only one single particle of partially burnt gunpowder were successfully extracted by SPME and analyzed by a gas chromatography coupled to a nitrogen phosphorus detector (GC-NPD). The results confirmed that the new extraction procedure is capable of extracting trace amount of MC and EC as signature molecules for the identification of GSR. The method represents a solvent-free extraction as a complementary analytical procedure for the forensic analysis of GSR-related evidences. The new extraction scheme with the capability of analyzing single particle of partially burnt gunpowder can also be applied to the identification of explosive residues, such as in post-blast investigations of improvised explosive devices.

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1. Introduction

Formulas of gunpowders vary based upon intended use, whether it is target practice, personal protection, hunting, etc. Despite the intended use of particular ammunition, contemporary gunpowders are designed with four categories of ingredients: explosives, plasticizers, stabilizers, and flash suppressors [1]. Ammunition makers may vary gunpowder compositions among all of the lines that each manufacturer sells, hence, every ammunition will contain a formula of components that are specific to them. Ideally, by identifying a profile of these components together in an unknown substance, examiners can determine the presence of or exclude the substance as gunshot residues (GSRs) or explosives. For example, Martz and Lasswell have used gas chromatography–mass spectrometry for the analysis of smokeless gunpowders in order to establish a database [2].

Forensic analysis of GSR samples includes microscopic examination, chemical testing, and analytical spectroscopy [3]. Currently, scanning electron microscope coupled to an energy dispersive X-ray detector (SEM/EDX) is the preferred confirmatory test associated with GSR analysis [4,5]. Combining morphologies and inorganic chemical compositions of GSR-like particles, one can determine the presence of GSR in the evidence. However, with the use of "lead-free" or "nontoxic" ammunitions, it is consequently difficult to prevent false negatives when searching for GSR by conventional SEM/EDX protocols [6]. To overcome this problem, detecting organic components of GSR (OGSR) has been sought.

The analysis of OGSR originating from the partially burnt gunpowder particles has gained a great interest within the forensic science community [7]. Muller et al. developed a novel method for the analysis of discharged smokeless power residues in order to estimate intermediate–long-firing range shootings [8]. Using a combination of alkaline hydrolysis with the Modified Griess Test, GC/MS, and GC/TEA analysis, chemical identification of gunpowder residues, as small as a single particle, collected by an adhesive lifter may be confirmed. Morales and Revilla V'azquez also developed a method that simultaneously detects inorganic and organic gunshot residues by using capillary electrophoresis [9]. Most of the organic stabilizers can be separated by the method. MacCrehan and Bedner analyzed significant additives to gunpowders by using both CE (capillary electrophoresis) and LC (liquid chromatography) [10]. The four key additives, nitroglycerin, diphenylamine, N-nitrosodiphenylamine, and ethyl centralite were analyzed as a mean of characterizing powders for source identification. Northrop et al. have also done extensive research on the analysis of OGSR [11–13]. Recently, Zhao et al. successfully detected trace methyl centralite and ethyl centralite from skins by desorption electrospray tandem mass spectroscopy (DESI-MSMS) [14]. Detection limits of 5–70 pg/cm^2 have been reported.

SPME (solid phase micro-extraction) is a solvent-free extraction technique that utilizes a thin solid phase coated on a fused

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silica fiber to absorb trace organic compound from samples [15]. Rodríguez et al. have evaluated the feasibility of SPME for the determination of organophosphorus flame-retardants and plasticizers in water samples by GC-NPD (gas chromatogram coupled with a nitrogen phosphorus detector) [16]. SPME–GC-NPD has been demonstrated a sensitive technique for detecting nitrogen containing compounds at sub-ppb level [17,18]. Applying SPME to extract signature molecules from the headspace of smokeless gunpowders has also been demonstrated by Furton and co-workers [19]. In this work, a new extraction scheme was designed for SPME–GC-NPD to analyze a single particle of partially burnt gunpowder collected near the target area from a close shot. The objective was to find a powerful alternative analytical method that is capable of recovering signature molecules for the determination of gunshot residues.

2. Materials and methods

2.1. Chemicals and samples

A manual SPME holder and fibers coated with polydimethylsiloxane (PDMS, 100 μm film thickness) were purchased from Supelco (Bellefonte, PA, USA). A bullet puller was obtained from a local sporting goods store in Houston, TX. A digital stirring hot plate was purchased from Fisher Scientific (Pittsburgh, PA, USA). Standard 2-mL glass vials with silicone septa and vacuum pump oil were purchased from Agilent (Santa Clara, CA, USA). The vacuum pump oil was used as an oil bath to maintain a constant extraction temperature during SPME. Standards of diphenylamine (DPA), 2-nitrodiphenylamine (2-NDPA), 4-nitrodiphenylamine (4-NDPA), 2-2, 2-4, and 4-4 dinitrodiphenylamine (2,2 DNDPA, 2,4 DNDPA, and 4,4 DNDPA) were purchased as a combined standard labeled ERG-006 from Cerilliant (Round Rock, TX, USA). Methyl centralite (MC) and ethyl centralite (EC) were purchased from Sigma–Aldrich (St Louis, MO, USA).

Five different kinds of ammunitions were used in this experiment. Winchester "Ranger" 9 mm (127 g, SXT +P+ model: RA9TA), CCI "Blazer Brass" 40 cal. (180 g, FMJ model: J01N3), Remington UMC 9 mm (115 g, FMJ model: L9MM3), Federal "Hydra-Shok" 40 cal. (135 g, JHP model: PD40HS4H), and Winchester "Personal Protection" 9 mm (143 g, JHP model: USA9JHP2). The firearms that were used were a Sig Pro (9 mm model 2009SP, semiautomatic) and a Beretta (model 96G 40 cal. semiautomatic).

2.2. Instrumentation

After SPME, all extracts were analyzed by a 7890A gas chromatograph (Agilent, Santa Clara, CA, USA) equipped with a split/splitless injector and a nitrogen phosphorous detector (NPD). A DB-5 ((5%-phenyl)-methylpolysiloxane) capillary columns (30 m × 0.25 mm i.d., 0.25 μm film thickness) was used through out the entire experiment. Helium (99.999%) was employed as carrier gas at a constant head column pressure of 96 kPa, and also as auxiliary gas in the NPD (3 mL/min). Auxillary air (99.995%) and hydrogen (99.999%) were used as detector gases at flows of 60 and 3 mL/min, respectively. Chromatographic separations were carried out at the initial temperature held at 40 °C for 2 min, then the temperature was ramped at 30 °C/min for 3 min and then 10 °C/min for 15 min to a final temperature of 280 °C held for 2 min. The injection was achieved by inserting the SPME fiber in the injection port for 2 min under the splitless mode. Injector and detector temperatures were set at 250 and 300 °C, respectively.

A digital microscope (Keyence Digital Microscope VHX-600, Woodcliff Lake, NJ, USA) was used to aid in the collection of partially burnt gunpowder particles from the target.

Fig. 1. Visual identification of partially burnt gunpowder particle was done at a high magnification (200×) under a Keyence digital microscope.

2.3. Gun shot residue sample collection

Firing of the ammunition samples was performed at the law enforcement training facility of the Huntsville Police Department in Huntsville, TX. Targets were pre-assembled in sterile laboratory conditions using a plain white T-shirt (100% cotton) and 14 cm × 18 cm pieces of thin cardboard. The T-shirts were cut at all seams and then cut to fit the cardboard backings. The cloth was then stapled using standard staples to the cardboard. Each target, once assembled, was placed into a sterile zip lock bag. The targets were shot at a distance of 5–6 cm to ensure that a large amount of residue would be collected. Once the gun was fired at the target, the target was then collected and placed back into its zip lock bag to await analysis.

2.4. Collection of partially burnt gunpowder

Each firearm was field stripped and cleaned using commercial gun cleaning solvents, and then rinsed with isopropyl alcohol to aid with drying. One shot was fired at each target and the barrels of the firearms were cleaned between each firing with cotton cleaning brush and solvent to prevent cross contamination between samples. The targets were then taken back to the lab for analysis. A high magnification digital microscope was used to locate and remove particulate samples. A typical partially burnt gunpowder particle at 200× is shown in Fig. 1. The particles were removed from the cloth using a sterile scalpel and needle. Single particles from each ammunition were then placed into separate 2-mL GC vials and capped with a septum cap to await SPME.

2.5. Un-burnt (unfired) powder sample collection

The un-burnt particles were collected by pulling a cartridge from the same box of ammunition as what was fired. A commercial bullet puller was used to extract the bullet from the cartridge. The powder contents were then emptied into a 2-mL GC vial for storage. Since gunpowder in a single cartridge may contain more than one type of gunpowder, before sampling, gunpowder grains from the same cartridge were microscopically examined to make sure they were similar in shape and size. To obtain representative gunpowder grain for each cartridge, three single powder grain samples were taken for analysis. The single particles were then placed into 2-mL GC vials separately to await extraction via SPME.