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Rapid Communication

Stability of smokeless powder compounds on collection devices

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ABSTRACT

The current trend towards the implementation of organic gunshot residue (OGSR) analysis into gunshot residue (GSR) investigation protocols typically involves the sequential analysis of inorganic and organic GSR. However, to allow for the consecutive analysis of inorganic and organic GSR, specimens will often be stored for different lengths of time which may result in compounds of interest degrading. In order to optimise storage conditions, it is important to consider compound degradation on collection devices during storage. This study investigated the degradation over time of compounds potentially present in smokeless powders and OGSR on two collection devices, alcohol swabs and GSR stubs. Over a period of 63 days, the highest degree of degradation was found in the first four days. Interestingly, energetic compounds were generally found to be more stable than smokeless powder additives such as stabilisers including diphenylamine and ethyl centralite, which might be problematic considering that these compounds are common targets for OGSR. The findings can provide valuable information to operational forensic laboratories to optimise their storage durations.

1. Introduction

The detection of compounds potentially present in smokeless powders plays an important role in the investigation of events involving the suspected use of firearms or explosives [1,2]. For firearm related events, burnt smokeless powders, so called organic gunshot residues (OGSR), and unburnt powders can assist in the reconstruction of events [3] and provide valuable information such as the estimation of the time since discharge [4–7], firing distance [8–10] or identification of a bullet hole [11]. Samples are commonly collected from the suspect, victim and surrounding objects using GSR stubs or swabs [12], whereby numerous factors influence the probability of detecting GSR on these collection devices. These include the time since discharge, environmental conditions during discharge, the weapon and ammunition used, collection efficiency and instrument limitations.

The increasing prevalence of heavy metal free ammunition has challenged the traditional analysis of GSR using only scanning electron microscopy with energy dispersive spectroscopy (SEM-EDX) [13–16]. Recent research efforts have focussed on the incorporation of OGSR analysis into standard operating protocols [15,17–20]. Using this approach, it is likely that an operational laboratory will be required to store specimens which could also influence the detection of OGSR.

Very few studies have investigated the influence of storage conditions on the degradation of smokeless powder compounds on collection devices. A study by Twibell et al. investigated the stability of nitroglycerin (NG) at different concentrations in eight solvents including acetone [21], which was identified as the superior extraction solvent from GSR stubs in a previous optimisation study [18]. Mean rates of loss were between 1%/day (for 8 ng/μL NG) and 3%/day (for 0.08 ng/μL NG). NG could not be detected in aqueous solutions, attributed to the presence and growth of microorganisms. Therefore, the addition of preservatives such as sodium azide or sodium metabisulfite was suggested [21]. A recent study evaluated the loss of various OGSR on swabs over 15 days during three different conditions, i.e. ambient temperature (20 °C), fridge (4 °C) and freezer (−20 °C) [17]. It was found that at a fixed temperature (such as ambient temperature) different compound families displayed vastly different degrees of decomposition, e.g. diphenylamine (DPA) and the its tested derivatives showed losses up to 40%, while other compound families showed different results. Furthermore, the storage temperature, i.e. ambient temperatures, fridge or freezer, impacted on the compound degradation in that storage in a fridge or freezer showed recoveries exceeding 95% and were therefore recommended for specimen storage [17]. However, a different study reported that degradation was observed even when samples were

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stored in a freezer [22], which could be attributed to different experimental designs [17].

In order to provide a recommendation for optimal specimen handling and storage, more information is required on the influence of storage conditions and durations on compounds present in smokeless powders degradation. To evaluate the impact of storage duration on collected specimens, a time study on the degradation of spiked smokeless powder compounds on two collection devices, GSR stubs and swabs, was conducted.

2. Materials and methods

2.1. Reagents and standards

The selected target analytes included a variety of compounds potentially present in smokeless powders, namely resorcinol, 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), tetryl, 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 4-amino-2,6-dinitrotoluene (4-A-2,6-DNT), NG, 1,3,5-trinitrobenzene (TNB), m-dinitrobenzene (m-DNB), DPA, *N*-nitrosodiphenylamine (*N*-nDPA), and ethyl centralite (EC), which were obtained from ChemService (West Chester, PA, USA) (TNT, 2,4-DNT, TNB, RDX, HMX, tetryl, TNB, m-DNB) and AccuStandard (New Haven, CT, USA) (resorcinol, DPA, *N*-nDPA, EC). 2-Naphthol (Dr. Ehrenstorfer; Augsburg, Bavaria, Germany) was employed as internal standard at a concentration of 20 ppm. Ultrapure grade water (18.2 $M\Omega\,cm^{-1}$) was obtained from a Sartorius 611 water purification system. Methyl *tert*-butyl ether (MTBE), acetone and acetonitrile (ACN) were purchased from ChemSupply Pty Ltd., Gillman, SA, Australia.

2.2. Instruments and conditions

The extracts were separated and identified using a previously developed and optimised gradient reversed phase method on an 1129 series high performance liquid chromatography (HPLC) system (Agilent Technologies) with UV detection at 214 and 254 nm [23]. A summary of the mobile phase gradient used is presented in Table S1 in the Supplementary material. The analytical column was a Zorbax RRHD Eclipse XDB-C18 3 × 100 mm, 1.8 μm column (Agilent Technologies) and was held at 43 °C during analysis. The flow rate was 0.800 mL/min, with a 1 μL injection volume. A 0.2 μm 1290 Infinity in-line filter (Agilent Technologies) was used for all analyses. Furthermore, an ultra high performance liquid chromatography (UHPLC) guard column (Eclipse, XDB-C18, 3.00 mm, 1.8 μm; Agilent Technologies) was used when GSR stub extracts were analysed.

Compound confirmation was achieved using a 6490 triple quadrupole mass spectrometer (MS) (Agilent Technologies) connected to an atmospheric pressure chemical ionisation ion source (G1947 A/B; Agilent Technologies). The instrument was controlled by MassHunter software version B.06.00 (Agilent Technologies) and was used in multiple reaction monitoring (MRM) mode. The MRM condition for the compounds of interest can be found in the Supplementary material Table S2 and in the Supplementary material of a previously published study [18].

2.3. Sample devices

Two different sampling devices were tested. For swabbing, alcohol swabs (Kendall medi wipes™) were used throughout all experiments. These wipes have previously been reported as suitable for the collection of organic explosives [24,25].

GSR stubs were purchased from Ted Pella Inc., USA. The stubs were already assembled consisting of a plastic holder with an aluminium stub with a double sided carbon tape on top (12 mm diameter) and a clear plastic cup to avoid contamination.

2.4. Experimental design

Swabs and GSR stubs were spiked with 10 ng (10 μL of a 1 ppm mixed standard solution in 50:50 ACN:MeOH) of the target compounds and left to dry. This amount was chosen as it represents relatively closely previously reported amounts of OGSR on collection devices [18,19] and it allows monitoring the stability of the target compounds over a relatively long time frame. Although spiking experiments do not fully represent the conditions in a real case scenario, this simplification was used in order to allow for sample standardisation and improved repeatability [17]. Following drying, spiked swabs and stubs as well as blanks were stored in scintillation vials in a refrigerator at 4 °C until extracted. On various days after the initial spiking, samples (in triplicates) and blanks were extracted following previously optimised extraction protocols [18].

In brief, swabs were sonicated in 5 mL MTBE for 5 min at ambient temperatures. After transferring the extract to another vial, it was dried down under a steady stream of nitrogen and reconstituted in 196 μL ACN:MeOH (50:50) and 4 μL internal standard (final concentration 20 ppm). A scheme of the experimental design involving alcohol swabs is presented in Fig. 1.

The GSR stubs were covered with 5.5 mL acetone, sonicated for 5 min at ambient temperature, with the extract dried under a steady stream of nitrogen. The residue was reconstituted in 196 μL ACN:MeOH (50:50) and 4 μL internal standard (final concentration

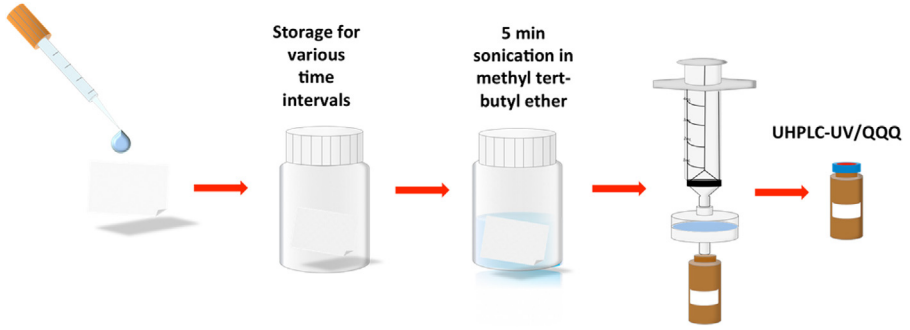

Fig. 1. Experimental design involving alcohol swabs. Alcohol swabs are spiked with a standard mixture (10 ng each) and left to try. Upon drying the swabs are stored in scintillation vials in a refrigerator at 4 °C. After various days (0, 1, 2, 4, 8, 15, 22, 29, 40, 49 and 63) the swabs are extracted by sonication using 5 mL MTBE for 5 min. The extracts are filtered, dried, reconstituted, and analysed using ultra high performance liquid chromatography coupled with UV and mass spectrometric detection.