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Establishing a universal swabbing and clean-up protocol for the combined recovery of organic and inorganic explosive residues

Nopporn Song-im [a,1], Sarah Benson [b], Chris Lennard [a,*]

[a] National Centre for Forensic Studies, University of Canberra, Canberra, ACT 2601, Australia
[b] Forensic and Data Centres, Australian Federal Police, GPO Box 401, Canberra, ACT 2601, Australia

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ABSTRACT

A single-step solvent extraction and a solid-phase extraction (SPE) clean-up procedure was developed and optimised in order to establish a universal sampling and clean-up protocol for the combined recovery of organic and inorganic explosive residues.

Mixtures of three common swabbing solvents (acetone, acetonitrile and methanol) with water, in various ratios, were assessed for the extraction of four target organic explosives [pentaerythritol tetranitrate (PETN), 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and triacetone triperoxide (TATP)] and two inorganic anions (chlorate and nitrate) from alcohol wipes that were used as a swabbing medium. An efficient, single-step extraction of both organic and inorganic compounds from the wipes was achieved using 60% v/v methanol/water.

To develop a clean-up procedure, four commercially available SPE cartridges (Oasis HLB, Isolute® C18, Bond-Elut® ENV and ABS ELUT Nexus) and an in-house packed XAD-7 cartridge were firstly evaluated for their retention capacity toward three organic explosives (PETN, TNT and RDX) in a mixture of methanol and water. A SPE technique was then developed and optimised from the short-listed sorbents with four representative organic explosives (including TATP). The Nexus cartridge was found to provide a suitable sorbent for extract clean-up following swab extraction with 60% v/v methanol/water. By incorporating the optimised clean-up procedure with the application of a polyester-based alcohol wipe as a sampling medium, a universal swabbing protocol for the combined recovery of both organic and inorganic explosive residues was established. The feasibility of the proposed protocol was assessed by collection and quantitation of the residue from a mixture of TNT, PETN and chlorate deposited on a laminate test surface.

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1. Introduction

Over the past decade, there has been a general development and optimisation of analytical methods targeting specific explosive residues. However, there is still a demand for a protocol optimised for recovering a wide range of explosives, including those traditionally encountered in casework (i.e., commercial and military explosives) and emerging threat materials such as organic peroxides and improvised organic/inorganic explosive mixtures.

The key to the successful detection of trace quantities of explosives in a highly contaminated environment not only relies on a suitable sampling method (e.g., swabbing) and a sensitive analytical technique, but also requires effective swab extraction and a compatible extract clean-up procedure. This is to ensure that all target explosives collected on the sampling medium are efficiently transferred into the extract and that co-extracted interfering compounds are removed before the extract is subjected to the final instrumental analysis.

By using a universal swabbing system, both organic and inorganic explosive residues can be targeted for collection on a single swab. The traditional sequential extraction method using different polarity solvents is not ideal, as the loss of certain compounds or groups of compounds is likely to occur, especially if an incorrect extraction sequence is applied. For the maximum benefit of utilising a universal swab, an effective single-step swab extraction for both organic and inorganic target compounds needs to be investigated and optimised.

The development of a universal swabbing protocol cannot be achieved without an associated procedure to clean up the swab extract. This crucial element of the protocol needs to be optimised to permit the purification and concentration of the analytes of

* Corresponding author. Tel.: +61 0 2 6201 2160; fax: +61 0 2 6201 2461.
E-mail addresses: nsong-im@chemcentre.wa.gov.au (N. Song-im), sarah.benson@afp.gov.au (S. Benson), chris.lennard@canberra.edu.au (C. Lennard).
[1] Current address: Forensic Science Laboratory, ChemCentre, PO Box 1250, Bentley Delivery Centre, WA 6983, Australia.

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interest while ensuring compatibility with the instrumental analysis methods commonly used for the detection and identification of explosive residues.

This study was comprised of three sections. The first part involved the determination of the optimum composition of mixtures of each of three organic solvents (i.e., acetone, acetonitrile and methanol) and water for the single-step extraction of both organic and inorganic explosives from the selected sampling medium (commercially-available alcohol wipes).

The second part of the project required the evaluation and optimisation of a clean-up procedure for the swab extracts utilising a solid-phase extraction (SPE) technique. In this study, a solid-phase extraction technique was not only applied for the removal of co-extracted interfering compounds and the pre-concentration of the compounds of interest, but also for the separation of the swab extract into organic and inorganic components for independent analyses. The concept is that the sorbent inside the SPE cartridge retains the organic explosive residues while the inorganic compounds pass through for collection and analysis. Washing solvents can then be flushed through the cartridge to remove interfering compounds and the organic explosives finally eluted from the cartridge with the aid of an eluting solvent. The use of SPE for the two functions of separation and clean-up of explosive extracts was first proposed by the Forensic Explosive Laboratory (FEL) in the UK [1]. The original FEL protocol used Chromosorb 104 as the SPE adsorbent [1,2]. A revised protocol utilising both Chromosorb 104 and Isolute ENV+, to incorporate the recovery of organic peroxides, has also been reported [3]. However, the Chromosorb porous polymer resin referred to in these publications had limited availability in Australia at the time of our study and, more recently, is no longer commercially available.

Four commercially available SPE cartridges – namely Oasis HLB, Isolute® C18, Bond-Elut® ENV and ABS ELUT Nexus – were evaluated and compared to results from cartridges packed with XAD-7, which were prepared in-house. Amberlite XAD-7 is an acrylate porous polymer. It was first introduced to recover organic explosives from hand swabs in 1982 by the Metropolitan Police Forensic Science Laboratory [4]. A further development of that method in 1985 introduced the use of a form of microcolumn extraction to make the process more convenient [5]. The work conducted by the Israel Police has also demonstrated the successful application of a microcolumn packed with XAD-7 for the purification of extracts recovered from post-explosion debris [6].

The recovery of explosive compounds using Oasis HLB (a copolymer between divinylbenzene and N-methylpyrrolidone) has already been investigated and it was found that this sorbent provides good retention of high polarity explosives, such as nitramines, with a cleaner extract compared to other SPE sorbents [7,8].

Although previous studies [8] have demonstrated the poor retention capacity of conventional C18 cartridges, the selected Isolute® C18 cartridge contained non-end-capped silica, which made it different from other C18s. It was envisaged that improved retention of polar organic compounds might be achievable with the additional interactions from the residual silanol group.

Bond-Elut® ENV is a high-purity styrene-divinylbenzene copolymer that the manufacturer claims has been optimised for the extraction of polar organic residues, including herbicides, metabolites and explosives. Also, many studies in the area of trace analysis of explosives in environmental samples have demonstrated the successful recovery of a wide range of explosives with this type of polymeric resin [9–11].

ABS ELUT Nexus is a copolymer between methyl methacrylate and divinylbenzene. To the best of our knowledge, Nexus is the only commercially available prepacked cartridge that contains an acrylate ester functional group, which is close to the functional group of XAD-7 resin. Also, several studies have demonstrated that this resin has the potential for use in the recovery of explosive compounds either in the gas or liquid phase [12,13].

To establish a universal swabbing and clean-up protocol, the single-step swab extraction and optimised clean-up procedure were combined with the findings from our previous study regarding the use of alcohol wipes as a universal swab [14].

The third and last section of the study served to demonstrate the feasibility of the proposed protocol via the recovery of a mixture of TNT, PETN and chlorate from a laminate test surface. A mixture of TNT, PETN and chlorate represents a combination of organic and inorganic compounds that may be encountered in an explosive device; for example, PETN from the detonating cord, TNT as the booster, and chlorate as a component of the main charge. A laminate surface was chosen due to its common occurrence in households and offices. In addition, there is limited information available regarding sampling from laminate surfaces when compared to other common surfaces such as glass and metal.

2. Materials and methods

2.1. Solid sorbents

Isolute® C18 500 mg packed in a 3 mL cartridge was supplied by BioLab Australia Pty., Ltd. (Scoresby, VIC, Australia). Bond-Elut® ENV 60 mg packed in a 3 mL cartridge and ABS ELUT Nexus 60 mg packed in a 3 mL cartridge both were purchased from Varian Australia Pty. Ltd. (Mulgrave, VIC, Australia). Oasis® HLB 60 mg packed in a 3 mL cartridge was purchased from Waters Australia (Rydalmere, NSW, Australia).

XAD-7 was purchased from Grace Davison Discovery Sciences (Rowville, VIC, Australia). The XAD-7 resin was washed by being suspended in deionised water with stirring for one hour. The water was then decanted and the resin suspended in methanol and stirred for another hour. After decanting the methanol, the washing process was repeated in the same manner with acetonitrile and then with acetone. After the final wash with acetone, the resin was allowed to dry in a fume cupboard overnight then the resin crushed and passed through a sieve. Only the resin with a particle size between 75 and 150 μm was selected (this was based on the findings published by Douse [5]). A 60 mg portion of the final resin was finally packed into a 4 mL Extract-Clean™ Empty SPE cartridge that was fitted with 10 μm PTFE frits. Both the empty cartridge and frits were obtained from Grace Davison Discovery Sciences. Although the empty cartridge was labelled as being 4 mL in size, after measuring the dimensions and volume of the packed cartridge, no difference was found in the volumes between the in-house packed XAD cartridge and the prepacked cartridges of other sorbents obtained from the vendors detailed above.

2.2. Reagents and standards

TNT (2,4,6-trinitrotoluene) was chosen as a representative nitroaromatic, PETN (pentaerythritol tetranitrate) as a representative nitrate ester, RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) as a representative nitramine, and TATP (triacetone triperoxide) as a representative organic peroxide. Chlorate and nitrate were selected as representative inorganic compounds relevant to explosive residue analysis.

Solutions of TNT, PETN and RDX, each at a certified concentration of 1000 μg/mL in acetonitrile, were obtained from ChemService (West Chester, PA, USA). TATP, at a certified concentration of 995 μg/mL in acetonitrile, was obtained from AccuStandard (New Haven, CT, USA).

2-Nitrotoluene (99.5% certified purity, obtained from ChemService, West Chester, PA, USA) was prepared as a 1000 ppm solution in LiChroSolv® acetonitrile (gradient grade for liquid chromatography, supplied by Merck, Kilsyth, VIC, Australia), and then an aliquot of this solution added as an internal standard for the quantitative analysis of samples containing both TNT and PETN during the feasibility study on the proposed universal swabbing protocol.

Sodium chlorate (99.8% purity) and ammonium nitrate (99.5% purity, ACS reagent grade), purchased from Sigma–Aldrich (Castle Hill, NSW, Australia), were used to prepare a stock solution of chlorate at a concentration of 2000 ppm in HPLC grade methanol and a stock solution of nitrate at a concentration of 3000 ppm in methanol, respectively. These standards were used for the investigation of a single-step swab extraction. The same stock solution of chlorate was also used to generate a deposit of mixed organic/inorganic compounds on the test surface for the evaluation of the proposed protocol.

High-purity water obtained from a Sartorius arium 611 water purification system, HPLC grade acetone (Lab-Scan Analytical Sciences, Bangkok, Thailand), HPLC grade acetonitrile (LiChroSolv®, Merck, Kilsyth, VIC, Australia), and HPLC grade methanol (Chem-Supply, Gillman, SA, Australia) were used to prepare the extraction solvents.

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