Science and Justice xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Science and Justice

journal homepage: www.elsevier.com/locate/scijus

Technical note

Investigating TNT loss between sample collection and analysis

Niamh Nic Daeid [a,*], Holly A. Yu [a,b], Matthew S. Beardah [c]

[a] Centre for Anatomy and Human Identification, School of Science and Engineering, University of Dundee, Dow Street, Dundee DD1 5EH, UK
[b] Department of Chemistry, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
[c] Defence Science and Technology Laboratory (Dstl), Fort Halstead, Sevenoaks, Kent TN14 7BP, UK

ARTICLE INFO

Article history:
Received 17 June 2016
Received in revised form 19 October 2016
Accepted 28 October 2016
Available online xxxx

Keywords:
Explosives
Forensic analysis
TNT
Post-blast
Proficiency test

ABSTRACT

Explosives residues are often collected from explosion scenes, and from surfaces suspected of being in contact with explosives, by swabbing with solvent-wetted cotton swabs. It is vital that any explosives traces present on the swabs are successfully extracted and detected when received in a laboratory. However, a 2007 proficiency test initiated by the European Network of Forensic Science Institutes (ENFSI) Expert Working Group on Explosives involving TNT-spiked cotton swabs highlighted that explosives may not always be detected from such samples. This paper outlines work performed to determine potential reasons for this finding. Cotton swabs were spiked using a solution of TNT and stored in nylon bags and glass vials for periods of 1, 2 and 4 weeks. Simulated swab extracts were also prepared and investigated. The samples were stored in a freezer, or at room temperature either in the dark or exposed to daylight. Overall, the cotton swabs stored at room temperature and exposed to daylight showed a very rapid loss of TNT over time, whereas cotton swabs stored in the freezer, and all simulated swab extracts, gave high recoveries over time. These results will be of benefit for practicing forensic explosives laboratories and for persons undertaking cold-case reviews involving explosive-based samples.

1. Introduction

The detection of trace (i.e. very low levels of) explosives during the investigation of an explosives-related incident can be of high forensic significance. It is therefore vital to be able to detect any traces of explosives present in samples submitted to a forensic laboratory. High explosives, such as TNT (2,4,6-trinitrotoluene), have limited non-explosives uses and a relatively low prevalence in the environment [1–3]. The detection of TNT can, as a consequence, be indicative of contact between a surface and an explosive, with a potentially unlawful origin [4,5], or can provide evidence of secondary transfer of such materials. On the other hand, a lower forensic significance may be assigned if low explosives constituents are detected, such as ammonium nitrate, as these may have an innocent origin (such as originating from fertilisers).

Following an explosion, intact explosives molecules and any degradation products will be widely scattered around the scene as explosives residues. These often have a low persistence in the environment and must be recovered rapidly [6]. Explosives residues are typically collected from post-explosion debris, as well as from other possible explosives sources, such as the hands or clothing of a suspect [4], by swabbing using cotton swabs wetted with an organic solvent [1]. Swab extracts may then be analysed using a variety of techniques, such as gas chromatography (GC)- and liquid chromatography (LC)-based techniques [4]. Currently there is no internationally agreed 'best practice' for exactly how to collect explosive residues by swabbing [7]. Due to the limited amount of literature investigating the stability of explosive materials on swabs and in solutions, forensic laboratories differ in their approach to storing samples from explosion scenes, and from surfaces suspected of being in contact with explosives.

When considering the potential forensic significance of detecting trace high explosives, it is of paramount importance that the detection and identification of explosives is reliable. If explosives residues are detected, knowledge of the type of explosives present may be sufficient to provide a link between a suspect and an explosion scene. Such evidence may subsequently be used in court, to describe the type of device used in a bombing [8]. For these reasons it is essential that high quality procedures are used during the detection and identification of trace high explosives [4].

One such example of an organic high explosive is TNT, used for both military and industrial applications (such as mining) [5]. TNT is cheap and safe to manufacture, safe to handle, has a high explosive power, good chemical stability and a low sensitivity to impact and friction [8,9]. For these reasons, TNT is a very commonly-used explosive.

In 2007, the European Network of Forensic Science Institutes (ENFSI) Expert Working Group on Explosives instigated an inter-laboratory proficiency test, where cotton swabs were spiked with a known quantity of TNT using a methanolic TNT solution to act as simulated explosion scene samples. The swabs were packaged in nylon bags and sent to member laboratories worldwide for the analysis and quantitation of

* Corresponding author.
E-mail address: n.nicdaeid@dundee.ac.uk (N. Nic Daeid).

http://dx.doi.org/10.1016/j.scijus.2016.10.007
1355-0306/

Please cite this article as: N. Nic Daeid, et al., Investigating TNT loss between sample collection and analysis, Sci. Justice (2016), http://dx.doi.org/10.1016/j.scijus.2016.10.007

any analytes present. Surprisingly, TNT was only detected by 5 out of 19 laboratories, at significantly lower levels than the initial spiked quantities [10]. This result was of concern, as it suggested that even if TNT traces are collected from a real-life explosion scene using a swab, they may not be detected during subsequent laboratory analyses, resulting in the potential to lose crucial investigative links.

A follow-up study was conducted by the UK Defence Science and Technology Laboratory (Dstl) in 2009 [11]. This involved spiking swabs with TNT and either analysing them immediately, or leaving them for a period of 5, 10 or 30 days before analysis. The study found significantly lower quantities of TNT were detected from the spiked samples compared to the initial spiked quantity. The loss of TNT appeared to be compounded with increased storage time between swab spiking and analysis, though no definitive conclusions were drawn for the low quantities of TNT detected. A further follow-up study was performed in 2009 [12]. This aimed to determine the effect of different solvents and packaging materials, and the effect of UV light, on samples containing TNT. The study tentatively identified three UV light-induced degradation products of TNT. Similarly, work by Song-im et al. investigated the stability of TNT extracts in a methanol:water mixture, finding that storage at low temperatures, and in a dark environment, was best [13]. However, less work has been done to determine the stability of TNT extracts in purely organic solvents, so we sought to explore this shortfall in the current work.

This paper presents work performed to follow up on the ENFSI results, to provide possible reasons for why the proficiency test gave such poor TNT detection. Several aims were identified for this work: to assess how TNT recovery from samples changes with increased storage time, to assess the effect of storage temperature on TNT recovery, to assess the effect of UV light exposure on TNT recovery, and to compare nylon bags and glass vials as storage containers for cotton swabs containing TNT residue. Cotton swabs were spiked with TNT using a solution of TNT in ethyl acetate. The swabs were packaged into nylon bags or glass vials and stored at room temperature in daylight, at room temperature in the dark, or in a freezer in the dark. Samples were prepared and stored for periods of 0 days (i.e. immediate analysis), 1 week, 2 weeks and 4 weeks. Additionally, simulated swab extracts containing TNT were produced in ethyl acetate and stored under the same conditions. The results showed that TNT on cotton swabs stored at room temperature and exposed to daylight underwent a very rapid loss over time, whereas cotton swabs stored in the freezer, and all simulated swab extracts, gave higher TNT recoveries even after 4 weeks. The study's results may be of use for those engaging in both the present-day analysis of explosives, and potentially for cold-case reviewers.

2. Experimental

2.1. Reagents and consumables

2,4-Dinitrotoluene (2,4-DNT) was obtained from Sigma Aldrich. Ampoules of 1000 μg/mL TNT in methanol were obtained from SPEX CertiPrep. Musk Tibetene (1-tert-butyl-3,4,5-trimethyl-2,6-dinitrobenzene) was obtained from Givaudan. GC-grade ethyl acetate was obtained from Sigma Aldrich. Nylon bags were supplied by Rilsan. Cotton ball swabs were Happy Shopper brand. 7 mL glass snap-cap vials were Samco brand. Clear glass GC vials were obtained from Chromacol.

2.2. GC–MS instrument and conditions

The GC–MS instrument consisted of an Agilent 6850 GC oven coupled to an Agilent 5795C VL MSD quadrupole with triple-axis detector. A 14 m silica BP5 column was used with a 0.25 mm i.d., coated with bonded 5% diphenyl-dimethylsiloxane at a 0.25 μm film thickness. The injector temperature was held at 175 °C and the oven temperature programme was 60 °C for 1 min, then increased at 20 °C/min to 200 °C for 2 min. The source used was electron impact, with 70 eV energy and a temperature of 230 °C. Masses were monitored between m/z 50–550.

2.3. Experimental conditions and parameters

Samples were stored as spiked cotton swabs in nylon bags or clear glass snap-cap vials, or as ethyl acetate extracts in clear glass vials. The swabs and extracts were either analysed immediately, or stored for periods of 1, 2 or 4 weeks. Once prepared, samples were stored in three different storage conditions: 1) In a cardboard box in a freezer, 2) At room temperature, on a bench top (exposed to ambient daylight), 3) At room temperature, stored in a dark cupboard. Room temperature samples were stored at temperatures ranging between 20 and 26 °C. Three replicates were prepared for each combination of conditions. A negative control was also prepared for each combination of conditions.

2.4. Experimental system development using 2,4-DNT

Initially, the use of a sonication step during swab extraction was considered. Using 2,4-dinitrotoluene (2,4-DNT) as an inexpensive TNT analogue, swab extractions were performed both with and without the use of a sonication step, to assess whether inclusion of a sonication step would be beneficial. For this, a 0.4 mg/mL 2,4-DNT spiking solution was prepared in ethyl acetate. Three sets of samples were prepared and analysed, with each set consisting of three replicates and a negative control. Two sets involved spiking cotton swabs using a solution of 2,4-DNT in ethyl acetate, and then extracting the swabs with or without a sonication step. The third set acted as a positive control, and involved extracting blank swabs, then spiking the 2,4-DNT solution into the blank extract.

For the 'sonicated' sample set, a clean cotton swab was placed into four glass vials. 0.5 mL of the 2,4-DNT spiking solution was spiked onto the surface of three of the swabs. The fourth swab was a negative control, and was not spiked. 4 mL ethyl acetate was added to each vial, and the vials were capped and sonicated for 10 min. After cooling to room temperature, each swab was pounded for 2 min using the tip of a Pasteur pipette, and the extract drawn up through the swab using a Pasteur pipette and transferred into a 5 mL volumetric flask. The swab was rinsed with a further 1 mL of ethyl acetate, and the washings added into the volumetric flask, before making up to 5 mL (some solvent was lost due to evaporation whilst pounding the swab). 100 μL of a 2 mg/mL solution of Musk Tibetine in ethyl acetate was added as an internal standard prior to GC–MS analysis.

The second set of samples was prepared in an analogous manner, but did not involve the 10-minute sonication step. The third set of samples were simulated swab extracts, and acted as a positive control with which to assess the recovery rate of the respective swab extractions: clean cotton swabs were placed into four glass vials. 4 mL ethyl acetate was added to each vial, and the vials were capped and sonicated for 10 min. After cooling to room temperature, each swab was pounded for 2 min using the tip of a Pasteur pipette, and the extract drawn through the swab using the pipette and transferred into a 5 mL volumetric flask. 0.5 mL of the 2,4-DNT spiking solution was added directly into three of the flasks (with one left blank as a negative control). Each flask was made up to 5 mL using ethyl acetate. 100 μL of a 2 mg/mL solution of Musk Tibetine in ethyl acetate was added as an internal standard prior to GC–MS analysis. Samples were injected in triplicate and the results averaged.

2.5. Validation of the developed experimental systems using TNT

After optimising the swab extraction procedure using 2,4-DNT, analogous extractions were performed with TNT. Due to the expense of the TNT standard compared to 2,4-DNT, the procedure was scaled-down: cotton swabs were divided into 5 pieces before use, with all cotton swab pieces weighing between 0.13 g and 0.16 g. The swabs were

Please cite this article as: N. Nic Daeid, et al., Investigating TNT loss between sample collection and analysis, Sci. Justice (2016), http://dx.doi.org/10.1016/j.scijus.2016.10.007