Forensic Science International 272 (2017) 159–170

Contents lists available at ScienceDirect

Forensic Science International

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

Time since discharge of 9 mm cartridges by headspace analysis, part 1: Comprehensive optimisation and validation of a headspace sorptive extraction (HSSE) method

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ARTICLE INFO

Article history:
Received 8 April 2016
Received in revised form 19 October 2016
Accepted 15 December 2016
Available online 24 December 2016

Keywords:
Forensic science
Firearm
Gunshot residue
Sorptive extraction
Design of experiments
Time since discharge

ABSTRACT

Estimating the time since discharge of spent cartridges can be a valuable tool in the forensic investigation of firearm-related crimes. To reach this aim, it was previously proposed that the decrease of volatile organic compounds released during discharge is monitored over time using non-destructive headspace extraction techniques. While promising results were obtained for large-calibre cartridges (e.g., shotgun shells), handgun calibres yielded unsatisfying results. In addition to the natural complexity of the specimen itself, these can also be attributed to some selective choices in the methods development. Thus, the present series of paper aimed to more systematically evaluate the potential of headspace analysis to estimate the time since discharge of cartridges through the use of more comprehensive analytical and interpretative techniques.

Specifically, in this first part, a method based on headspace sorptive extraction (HSSE) was comprehensively optimised and validated, as the latter recently proved to be a more efficient alternative than previous approaches. For this purpose, 29 volatile organic compounds were preliminary selected on the basis of previous works. A multivariate statistical approach based on design of experiments (DOE) was used to optimise variables potentially involved in interaction effects. Introduction of deuterated analogues in sampling vials was also investigated as strategy to account for analytical variations. Analysis was carried out by selected ion mode, gas chromatography coupled to mass spectrometry (GC–MS). Results showed good chromatographic resolution as well as detection limits and peak area repeatability. Application to 9 mm spent cartridges confirmed that the use of co-extracted internal standards allowed for improved reproducibility of the measured signals. The validated method will be applied in the second part of this work to estimate the time since discharge of 9 mm spent cartridges using multivariate models.

1. Introduction

In the forensic investigation of firearms-related cases, law enforcement authorities often require evidence to link a firearm seized on a suspect to spent cartridges found at the crime scene. This generally involves mark comparisons between reference and indicial material in order to reveal common patterns between physical characteristics [1]. In some cases, however, the defence does not directly contest the source of the questioned spent cartridge, but rather its relevance, by arguing that it had been fired for legitimate reasons prior or after to the occurrence of the alleged crime [2,3]. If such allegations are forwarded, estimating the time since discharge might be particularly useful in helping the justice with the decision-making process [4].

A promising approach towards achieving this is to monitor (over time) the decrease of selected volatile organic substances formed during the discharge, i.e. gunshot residue (GSR) [5–9]. An especially heterogeneous mixture, GSR is composed of metallic micro-particles, unburnt or partially burnt smokeless powder flakes and explosion products [10–13]. Explosion products include light di- and tri-atomic molecules (e.g., H_2O, CO, CO_2, H_2 and N_2), derivatives of benzene (e.g., benzonitrile and tolunitrile) and polycyclic aromatic hydrocarbons (PAHs) (e.g., naphthalene,

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http://dx.doi.org/10.1016/j.forsciint.2016.12.029
0379-0738/

acenaphthene and pyrene) [14–18]. Given their significant vapour pressures, these are volatile and disappear over time after the cartridge is fired through evaporation and diffusion phenomena [15]. Application of solid phase micro-extraction (SPME) as a sampling technique to recover and analyse these explosion products was first suggested by Andrasko and Stahling [19] in 1999, following the encouraging results obtained on shotguns [16]. Specifically, the original protocol involved extracting the residual amounts daily from the internal atmosphere of the questioned spent cartridge until the total disappearance of any response after gas chromatographic analysis [19]. Naphthalene and an unidentified decomposition product of nitrocellulose (referred as “TEA2”) were then exploited as target analytes to make a decision about the time elapsed since discharge. However, while partial ageing curves could be obtained using this multiple-sampling procedure, the underlying premise relied on the fact that SPME did not significantly modify the cartridge’s internal atmosphere [20]. Subsequent studies proved otherwise for small calibres [17], making it impossible to compare the obtained partial ageing profiles with reference curves acquired from analogue cartridges sampled immediately after discharge. In order to solve this problem, a single-extraction approach was later evaluated by Weyermann et al. [17], which avoided interferences between samples. Nonetheless, it also showed that the amounts detected in different cartridges were seldom reproducible and that largely imprecise time-since-discharge estimates were obtained. Hence, no reliable approach is currently available to deal with these kind of appraisals.

In tracking down the causes of these issues, the natural complexity of the specimens themselves can certainly be a contributing factor. Indeed, spent handgun cases are difficult supports which, due to their limited surfaces and small volumes, do not allow deposition of large amounts of GSR. Moreover, variations in the explosion conditions during firing are surely prone to introduce shot-to-shot variability in released amounts of GSR. Beyond these typically forensic problems, however, three additional factors can also explain current limitations: the extraction technique, the targeted compounds and the interpretation models. Since its first implementation in the analysis of volatile GSR fraction, SPME has been the extraction technique of choice due to its low invasiveness and exhaustiveness, which allowed sequential sampling of the same specimen [16]. However, these characteristics are also its main drawback, as they could make the technique scarcely efficient (both in terms of repeatability and limits of detection) on diluted samples, such as headspaces of spent cases. Furthermore, most of the works in the field essentially focused on a small set of compounds with relatively high volatility (e.g., naphthalene) and few attempts have been made to simultaneously consider the whole available chemical information in a unique interpretative model. In this regard, it should actually be noted that most published dating approaches were essentially based on the assessment of one compound at the time through very simplistic (and often, not statistically-based) techniques.

Consequently, the present series of paper aimed to more systematically evaluate the possibility of using headspace analysis of spent handgun cartridges to provide helpful dating evidence through the use of more efficient analytical and interpretative tools. The main purpose of this first part was to address analytical questions and, specifically, to optimise an enhanced multi-residue (instead of a single-analyte) method to obtain a more comprehensive overview of the ageing processes in spent cartridges. In this regard, headspace sorptive extraction (HSSE) recently proved to be a more efficient in comparison to SPME for the analysis of volatile GSR in spent cases [21], and was thus adopted. Indeed, HSSE involves the use of a stir bar coated with a layer of polydimethylsiloxane (PDMS), which is significantly thicker in comparison to SPME fibres. As a result, better recovery yields are generally achieved, benefitting detection limits and repeatability; a higher number of compounds are also generally co-extracted, providing an opportunity to follow the evolution of a greater number of molecules with a more diverse volatility range [15,21]. Thus, 29 compounds known to be released during a cartridge discharge were selected as targets on the basis of previous studies [15,21] and their chromatographic separation was optimised by liquid injection of a mixture of standards. A selected ion mode approach was implemented, which involved a short run time while maintaining good chromatographic resolution. Then, HSSE extraction and desorption parameters were tuned by extracting blank cartridges spiked with known amounts of analytes. Introduction to the sampling vials of deuterated analogues before extraction was also investigated to account for analytical variations and to allow for a semi-quantitative approach. The following parameters were optimised: HSSE stir bar type, spiking method (solvent and volume), extraction conditions (temperature and time) and thermal desorption conditions (desorption temperature, time, gas flow and cryo-focusing temperature). The effect of each parameter on the chromatographic step was studied and a multivariate statistical approach was adopted for their optimisation. Experiments were thus carried out following precise designs of experiments (DOE) [22–25], which involved the simultaneous variation of all the parameters over their experimental ranges. The advantage of DOE over the traditional one-variable-at-time optimisation method resides in its ability to account for interactions between the different variables and to construct response surfaces, which are helpful tools for selecting optimal analytical conditions. The optimised method was finally validated and applied to the analysis of real 9 mm spent cartridges.

2. Material and methods

2.1. Materials

Based on previous research [15,21], 29 target compounds known to be interesting target analytes for dating were selected (Table 1). Of the selected compounds, 26 were explosion products frequently found after the discharge of handgun cartridges and the remaining 3 were additives of smokeless powders. Additionally, 5 deuterated molecules were added as internal standards and 24 molecules normally co-extracted with target analytes from spent cartridges were used in some experiments for the optimisation of the chromatographic method and the estimation of the global selectivity. Table S1 in Electronic Supporting Material (ESM) shows the list of all these compounds, complete with manufacturer information. Solvents used include dichloromethane (Sigma-Aldrich), acetone (Sigma-Aldrich), diethyl ether (Fluka) and methanol (Sigma-Aldrich), all of analytical grade. For each substance, a standard stock solution was prepared at a concentration of 1 mg mL^{-1} in dichloromethane. Working solutions for the various experiments were prepared from successive mixtures and dilutions of these stock solutions. Ammunition used was 9 mm Parabellum from Geco (RUAG Ammotec, Thun, Switzerland).

2.2. Preparation of blank cartridges

Spiking blank cartridges (i.e., blank matrices) with known amounts of target compounds was necessary for the purpose of optimisation. Blank cartridges were obtained by extracting previously discharged 9 mm cartridges in an ultrasonic bath using the following solvents: acetone, methanol and dichloromethane. For each solvent, two successive 15 min extractions were carried