FORENSIC SCIENCE JOURNAL SINCE 2002

Forensic Science Journal
2024;23(1):1-10
fsjournal.cpu.edu.tw
DOI:10.6593/FSJ.202412_23(1).0001

Forensic Profiling of Gunshot Residues from Spent Cartridge Cases by Solid Phase Microextraction-Gas Chromatography-Mass Spectrometry

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Received: 3 November 2023; Received in revised form 12 May 2024; Accepted 12 June 2024

Abstract

Gunshot residues (GSR) produced from different ammunitions upon firing using the same firearm could be varied according to the compositional ingredients used to make the propellant powder. Due to the introduction of non-toxic ammunition, the conventional detection of lead, barium and antimony has also reported obstacles for the confirmative determination of GSR. In such cases, the organic profiles of GSR could serve as the supporting evidence to prove a firing activity and to differentiate the ammunitions. This study was aimed to profile the organic GSR from spent cartridge cases by solid phase microextraction-gas chromatography-mass spectrometry (SPME-GC-MS) for forensic comparison. In this study, eleven spent cartridges were subjected to SPME-GC-MS and the chemical attribution signatures in each profile were identified. Subsequently, the organic GSR profiles across various ammunition types were compared, and a screening methodology for classification of GSR profiles was proposed. Our SPME-GC-MS analysis on the spent cartridge cases had detected five key compounds, namely the diphenylamine, dibutyl phthalate, ethyl centralite, tributyl acetylcitrate, and butyl citrate, that possessed important roles in propellant powders. Comparison of organic GSR profiles revealed that the choice of stabilisers and plasticisers used were found to be varied among manufacturers. Based on the proposed screening methodology, five distinct categories were formed. By applying such screening methodology, unknown samples could be associated with potential ammunition types or distinguished based on the specific sources. To conclude, the study had successfully profile the organic GSR from spent cartridge cases, and the screening methodology could serve as a useful tool to classify and distinguish GSR samples, assisting forensic investigation in criminal cases involving firearm.

Keywords: gunshot residue, spent cartridge cases, organic gunshot residue, solid phase microextraction (SPME), gas chromatography-mass spectrometry (GC-MS)

Introduction

Gunshot residue (GSR) is the trace evidence that assists forensic experts in resolving cases involving firearms. It can be found on the skin, hair, body parts, clothing of the shooter, and the immediate surroundings of the incident [1]. Such residue may also be transferred through contact with items like fired weapons, spent cartridge cases, or contaminated surfaces. From the forensic science perspective, the existence of GSR on a sample may provide additional evidence supporting that a surface could have been involved being near a firearm discharge, having a connection to firearms, or recently touching a contaminated surface [2].

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GSR comprises two main components, namely the organic GSR (OGSR) and inorganic GSR (IGSR), arising from different parts of an ammunition. OGSR compounds could probably be originated from the propellant and lubricant of a firearm, whereas IGSR particulates could be contributed by the propellant, primer, bullet, and cartridge case [3]. The organic component detail including diphenylamine (DPA), nitrocellulose (NC), nitroglycerine (NG), ethyl centralite (EC) could be helpful in identifying the criminal case [4].

Solid phase microextraction (SPME) is a simple and straightforward extraction technique which had been applied in the detection of GSR. Involving no solvent, it serves to be environmentally friendly and allows for the extraction of organic compounds at trace levels from solid, liquid, or gas samples [5]. Such technique had been applied for the detection of organic compounds in smokeless powders [6-8], as well as the residues left in the spent cartridge cases [9,10] and from the shooter hands [11], showing good recovery efficiency. Upon extraction by SPME, the samples could be further analysed by gas chromatography (GC), particularly coupled with mass spectrometry (MS) for identification [6,10,11].

Introduction of heavy-metal free ammunition has led to the need to screen for OGSR. Currently, analytical efforts are divided into the analyses of IGSR and OGSR. In fact, the determination of IGSR continues to the be gold standard for the confirmation of GSR particles. However, the analysis of OGSR could serve to support the IGSR profiles where they might not be conclusive enough for confirmation especially due to the shift of primer composition in the ammunition. In this context, GC-MS has shown promising results for OSGR determination. Its availability of instrumentation and ability to analyse wide range of OGSR relevant analytes further supports its potential in this field [8,10,12,13]. Its application could offer fair delivery of justice, providing valuable insights in firearm-related cases. It was also noted that traditional methods of GSR detection, particularly utilising liquid-liquid extraction and/or dissolution of recovered sample into solution form, have encountered challenges related to the speed of sample preparation step and analysis, and adaptability to new types of ammunition [14].

In recent years, there has been a growing interest in analysing organic compounds in GSR. Research trends are now focused on developing a complementary examination based on organic residue, which could offer the advantages of broadening the range of target traces that can be detected. Through an established method for the analysis of OGSR, compounds that make up a significant percentage of the propellant could be detected after discharge compared to those present in trace amounts. Apart from that, the compounds unique to propellant manufacture and have no potential alternative sources could also ensure a higher level of confidence in their association with GSR [15].

This research study assisted the identification of OGSR profiles from different types of ammunition recovered at crime scenes. Chemical attribution signatures originated from propellant powders holds great potential in forensic science to compare among ammunitions, especially from those which illegally manufactured. The proposed screening methodology could also be utilised to determine or exclude specific ammunitions, aiding the forensic investigation of firearm-related cases.

Materials and methods

Spent cartridge case samples

Eleven types of 9 mm calibre ammunition were supplied by the Royal Malaysia Police as follows:

A. Arms Corporation (Full Metal Jacket [FMJ], round nose, 124 gr, Marikina City, Philippines)
B. SME (FMJ, Round Nose, 115 gr, Selangor, Malaysia)
C. Inceptor-Polycase (Advance Rotation Extreme (ARX), 65 gr, Georgia, United States)
D. Ruag Ammotech (Jacketed Deform Projectile (JDP), Round Nose, 99 gr, Bern, Switzerland)
E. Sellier and Bellot (Jacketed Hollow Point (JHP), 115 gr, Prague, Czech Republic)
F. GECO (Hexagon [HEX], 124 gr, Troisdorf, Germany)
G. Bullet Master Co. (Lead Round Nose [LRN)], 135 gr, Kanchanaburi, Thailand)
H. Sellier and Bellot (FMJ, round nose, 115 gr, Prague, Czech Republic)
I. Arms Corporation (JHP, 115 gr, Marikina City, Philippines)
J. Royal ammunition Co. (JHP, 115 gr, Nakhon Sawan, Thailand)

K. Remington Arms Company (JHP, 115 gr, Connecticut, United States)

Each individual spent cartridge case was kept in 10 mL headspace vials with screw caps (Supelco, Sigma Aldrich, St. Louis, MO, USA).

Solid-phase microextraction procedure

A manual SPME holder and SPME fibre coated with 85 µm polyacrylate were used in the experiment. The SPME extraction parameters were set based on a previous study [8]. During the extraction, spent cartridge case in the vial was placed horizontally with screw cap closed tightly in an oven. The vial with cartridge case was incubated for 2 min at 66°C. The needle was then penetrated through the septum of screw cap, exposing coated fibre to the headspace of the vial. The fibre was handled carefully to avoid contact with the spent cartridge case or the wall of vial. The coated fibre was then reinserted into the needle upon extraction for 21 min. After the extraction procedure, the coated fibre was then introduced into GC-MS for analysis.

Instrumental conditions

Analysis of GSR from spent cartridge cases was adapted from Chang et al. [8] using a 7890B gas chromatography (GC) system equipped with a split/splitless injector and mass spectrophotometer (MS) from Agilent Technologies, located in our forensic laboratory. Chromatography employed an HP-5 capillary column (0.25mm × 30m × 0.25 µm) obtained from Agilent Technologies (Santa Clara, CA, USA). Purified helium gas (99.997%) served as the carrier gas at a constant flow rate of 0.5 mL/min. Injection in splitless mode was performed at an inlet temperature of 250 °C. The initial oven temperature was set at 125 °C, ramped at a rate of 4 °C/min to 260 °C, and held for 2 min. The detector operated at 300 °C. GC automation and data analysis were operated using MassHunter Workstation software (Agilent Technologies, Santa Clara, CA, USA).

Organic GSR analysis from spent cartridge cases

A total of eleven spent cartridge cases collected in separated vials were used for the experiment. Each spent cartridge case was subjected to SPME-GC-MS. Each sample was conducted with triplicate analysis to ensure the reproducibility of repeated SPME procedures. The source and function of detected substances were compared with relevant literature. Subsequently, the presence of each detected substance was compared among the eleven spent cartridge case samples.

Proposal of screening methodology

A screening methodology was proposed through a comparison and classification of the prevalence of organic substances found in each spent cartridge case profile, ranging from the most frequently detected to the least. A flowchart was used to illustrate the screening methodology for the categorisation and differentiation GSR samples. Lastly, all the eleven spent cartridge case samples tested in this study were categorised into different groups using the proposed screening methodology.

Results and discussion

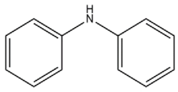
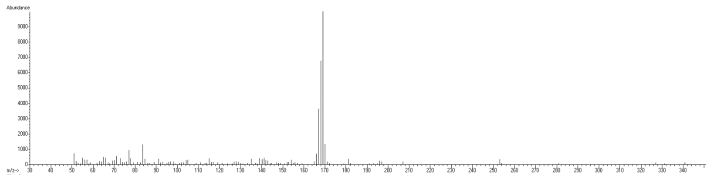
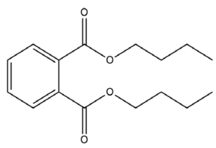
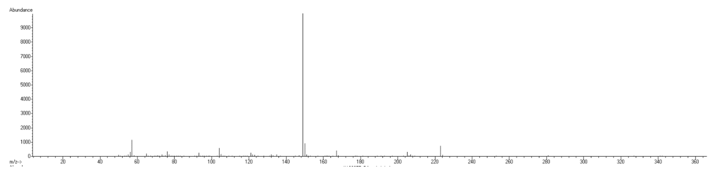
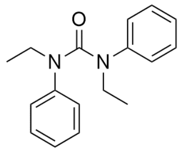
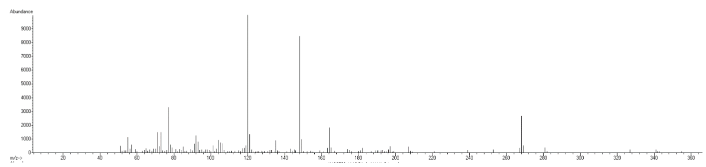
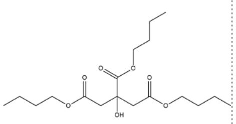
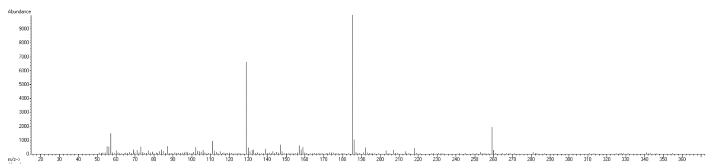
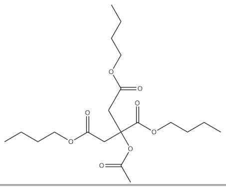
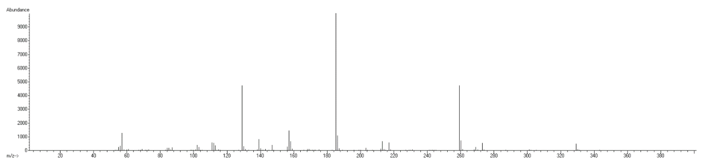
Reproducibility of repeated SPME procedures

In this study, the reproducibility of three SPME injections were investigated to check if the different sample preparation steps could produce reproducible results. Sample A was chosen as the representative sample, and the presence of dibutyl phthalate (DBP) peak at the retention time 18.878 min was found in all three chromatograms. Based on the peak areas of DBP in each chromatogram, the percentage of relative standard deviation (%RSD) was calculated by expressing standard deviation as a percentage of the mean of data. The %RSD for DBP in Sample A was determined to be 8.31%, indicating a good level of variability around the mean.

Substance identification in GSR samples

Upon a firearm discharge, NC and NG tend to undergo decomposition, restricting their detection in GSR [16]. This was also supported by previous studies where stabilisers and plasticisers were the common target analytes whenever GSR was encountered [10,11]. In this study, the analysis of eleven spent cartridge case samples yielded a total of five identified compounds. The identified compounds among the eleven samples included diphenylamine (DPA), dibutyl phthalate (DBP), ethyl centralite (EC), butyl citrate, and tributyl acetylcitrate (TAC). These substances were found to carry their respective functions in smokeless powder based on the literature search. The peaks appearing in mass spectra of these five substances in relation to their respective m/z were also investigated and summarised in Table 1.

Table 1 Structure, mass spectra, and mass to charge ratio (m/z) for five identified compounds.

Compounds	Structure	Mass Spectrum	Mass to Charge Ratio (m/z)
Diphenylamine			170, 169, 84, 77, 66, and 51.
Dibutyl phthalate			223, 205, 149, 104, and 57.
Ethyl centralite			269, 148, 120, 104, 92, 77, and 51.
Butyl citrate			361, 259, 185, 129, 111, and 57.
Tributyl acetylcitrate			403, 259, 185, 158, 129, and 57.

Based on the identified compounds, DPA is a stabiliser originated from propellant powder [10,17,18]. Propellants which contain NC may undergo continuous decomposition and further release the decomposition products that accelerate the decomposition process. Therefore, stabiliser is incorporated into the NC/NG-based propellant to prevent such self-accelerating behaviour. In other words, stabilisers act to capture the nitrous decomposition products and further form a stable compound, thereby preventing and delaying the further decomposition.

DBP is a plasticiser which is commonly found in ammunition, and its appearance in GSR is originated from the propellant powder [17,19]. Plasticisers are additives that could be detected from gunshot residue samples [4]. In gun propellant, plasticisers play important role in controlling the mechanical properties and contributing to the homogeneity and plasticity of the propellant dough, further facilitating the propellant processing. Other than that, organic phthalates such as dioctyl-phthalate and dioctyl-adipate have also been widely used as plasticisers in conventional gun propellant [20]; however, they were not detected in the eleven GSR samples tested in this study.

Other than that, EC was derived from the propellant powder. Similar to DPA, it acted as a stabiliser in ammunition [10,17,18]. EC is classified as a first-category compound due to its high affinity for GSR and limited usage other than GSR-related applications. On the other hand, DPA and its nitro-derivatives are fall under the second-category compounds as they exhibited a strong association with GSR while also having broader applications beyond GSR-related contexts [21]. For example, DPA and its derivatives were reported with their applications as antioxidants in the rubber and elastomer industry. DPA was also extensively utilised to prevent post-harvest deterioration in crops, and it played a role in the production of dyes and pharmaceuticals [22].

Butyl citrate could serve as both moderant and plasticiser which influence the burning behaviour of smokeless powder. As a result, it has the potential to be used as an alternative to commonly used plasticisers like phthalates [23]. Recently, Gańczyk-Specjalska et al. [24] conducted a study to investigate the effect of citrate plasticisers on the properties of NC granules. Their research proposed the use of butyl citrate as a non-toxic plasticiser to replace traditional options like DBP. The study also suggested that citrate plasticisers could significantly enhance the mechanical properties of NC granules, including their hardness and elasticity. Additionally, these citrate plasticisers could also reduce the sensitivity of NC to impact and friction.

TAC was reported to be widely used as a substitute plasticiser for phthalates. Fryš et al. [25] stated TAC as one of the components to be detected in double-base propellant. In their study, they had presented a method for focused ultrasonic extraction of NG, triphenylamine, and TAC from double-base propellant samples, followed by GC-MS. Research conducted by Mendonça-Filho et al. [26] highlighted TAC as a promising and non-toxic candidate for replacing DBP in propellant compositions. The study evaluated the toxicity, performance, and erosivity of NC-based propellants with and without TAC, demonstrating its potential as a safer alternative. Similarly, Gańczyk-Specjalska et al. [24] proposed the use of TAC as non-toxic plasticisers to replace the traditional plasticisers.

Distribution of OGSR in the eleven cartridge case samples

The identified OGSR compounds from the samples were categorised based on their respective functions, and their distribution is depicted in Table 2. Among the samples, the most prevalent OGSR compound was DBP, existing in all eleven tested samples. On the other hand, the least frequently observed compound was butyl citrate, detected in one sample, contributed to only 9.09% among the samples.

Table 2 Distribution of stabilisers and plasticisers among the eleven cartridge case samples.

Sample	Stabiliser		Plasticiser		
	Diphenylamine	Ethyl centralite	Dibutyl phthalate	Butyl citrate	Tributyl acetylcitrate
A	√		√		
B	√		√		
C			√		
D	√	√	√		
E	√		√		
F	√	√	√		
G			√		
H	√		√		
I	√		√	√	√
J			√		√
K			√		√

√ indicates the presence of compounds in the spent cartridge case

Stabilisers

Focusing on the distribution of stabilisers, four samples (36.36%) did not show any presence of stabilisers, including both DPA and EC. On the other hand, the presence of both DPA and EC stabilisers were observed in two samples (18.18%), while DPA alone was present in five samples (45.45%). It was highlighted that DPA was the most common stabiliser in OGSR among the samples.

As a stabiliser, the presence of DPA alone might not provide conclusive evidence of a gunshot discharge. This was because the industrial and environmental applications of DPA typically do not involve the use of nitrating agents [27]. DPA is only considered in conjunction with its nitrated derivatives due to its relatively higher occurrence in occupational and environmental settings. Therefore, it is crucial to consider the presence of all OGSR compounds to accurately profile different types of bullets. The detection of a wider range of OGSR compounds provides more specific and informative data [28]. However, the nitrate-derivatives of DPA were not detected in the tested samples, probably due to its very low concentration especially after combustion at very high temperature.

On the other hand, EC is an additive used in double base propellant powders for firearms and rocket. It was classified as a compound that was strongly associated with GSR as it possessed very limited applications which was unrelated to GSR. Along with DPA with good association with GSR but with a wider range of applications beyond GSR analysis, it could highlight the significance of DPA and EC in the identification and analysis of GSR materials [29].

The absence of stabilisers did not necessarily rule out the presence of GSR, as other components may still be present [30]. The undetectable stabilisers could be due to the low concentration of the substances, completely consumption during the combustion, or usage of other stabilisers instead of DPA and EC. Other than that, reactions with stabilisers might occur during ammunition storage and therefore it could be a sign of improper storage or an extended storage of ammunition prior to firing [17,31]. The absence of stabilisers should be considered in conjunction with other evidence in forensic analysis GSR analysis is a multi-faceted process that involves the examination of various components, including inorganic and organic residues.

Plasticisers

All eleven samples (100%) showed the presence of plasticiser, particularly the DBP. On the other hand, the presence of TAC was observed in three samples (27.27%), while butyl citrate was found to be present in one sample (9.09%). Carrying mechanical properties, plasticisers with its viscosity could allow for easier mixing and further providing a longer pot life. When plasticisers were incorporated into polymers, it penetrated the matrix and reduced the cohesive forces, increasing the free volume. This enhanced segment mobility resulting in the low glass transition temperature, indicating the effectiveness of the plasticisers. The inert or non-explosive plasticisers are typically high molecular weight esters that were compatible with NC and NG. These plasticisers which were typically high boiling liquids served various purposes such as reducing the NG sensitivity, improving propellant's mechanical properties, adjusting energy levels and burn rates, modifying processing characteristics, and balancing oxygen content. DBP is commonly used as inert plasticisers with resinous binder material.

According to Goudsmits et al. [29], phthalates are commonly used to distinguish between different propellant powders or GSR samples as well as for the study on time since discharge. Although DBP is often associated with OGSR materials, its widespread prevalence diminishes its strong association with GSR compounds due to its common occurrence in the environment [28]. Recent studies have highlighted the use of butyl citrate and TAC as the eco-friendly alternatives to phthalates plasticisers like DBP. Wang et al. [32] and Gańczyk-Specjalska et al. [24] had proposed butyl citrate as a new eco-friendly inert plasticiser substitute for phthalate derivatives. Similarly, in the study by Fryš et al. [25], TAC was identified as a component in double-base propellant. Mendonça-Filho et al. [26] also mentioned that TAC was a promising nontoxic candidate to replace DBP in propellant.

It was worth noticed that multiple plasticisers were found in a single GSR sample. A study on the structure and properties of propellant based on NG/glycerol triacetate mixed plasticisers found that the ductility of the propellant could be improved, implying that the mixed plasticisers made an effective propellant powder [33]. Thus, the presence of butyl citrate and/or TAC as demonstrated in the three samples together with DBP simultaneously was common.

Establishment of screening protocol

The detected OGSR compounds were used to compare and classify OGSR profiles from different types of ammunition. The flowchart shown in the Fig. 1 demonstrates a screening methodology for the classification and discrimination of GSR samples based on their OGSR profiles.

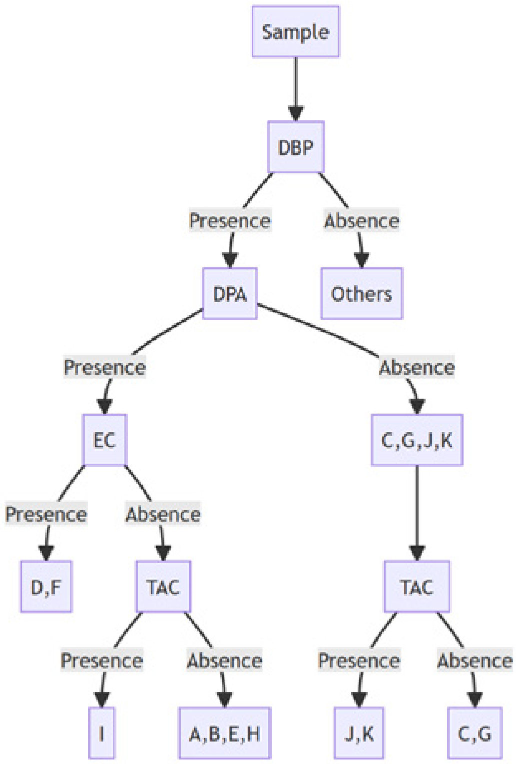


Fig. 1 Flowchart for the classification of OGSR compounds.

To begin the classification procedure for an unknown sample, the presence or absence DBP shall be initially assessed. If DBP was detected in the sample, it shall be proceeded to the comparison with the next. On the other hand, if it was not present, it could be suggested that the sample might have originated from a different type of ammunition not included among the eleven types tested in this study. The similar procedure shall be proceeded until the determination on the presence of TAC. Through this approach, forensic investigators could systematically determine the presence or absence of specific compounds in unknown samples, potentially linking them to distinct types of ammunition or distinguishing them from other particular sources. This approach would allow for the comparison of the OGSR profiles, aiding in the forensic analysis of gunshot-related incidents.

In the context of a crime scene, the analysis of OGSR from spent cartridge cases could provide insights into the type of ammunition used, aiding in the reconstruction of events. Similarly, it could be instrumental in establishing the recent discharge of firearms, helping to identify potential suspects. The ability to differentiate between various ammunition sources added another layer of investigative depth, potentially associating a specific weapon or source with a given crime. Comparing the OGSR profiles across different crime scenes could also help establishing links between seemingly unrelated cases, providing a comprehensive overview of broader criminal activities.

Comparison of GSR profiles

In this study, the eleven samples were classified into five distinct categories based on the detected OGSR compounds and the screening methodology. These categories were defined as demonstrated in Table 3. No discernible connections emerged among the five categories with respect to their manufacturer, country of origin, or nose type. Notably, Category 1 (Sample D and F) and Category 5 (Sample C and G) exhibited distinctive profiles, while Category 2 contained one solitary sample, rendering meaningful comparisons unfeasible. Within Category 3, three samples were identified as FMJ type ammunition (Sample A, B, and H), with Samples E and H sharing the same manufacturer, Sellier and Bellot, from the Czech Republic. Lastly, Category 4 was characterised by samples sharing a common nose type, specifically JHP.

Table 3 Comparisons of GSR profiles based on five classifications.

Category	Sample	Manufacturer	Country of origin	Nose type
1	D	Ruag Ammotech	Switzerland	JDP
	F	GECO	Germany	HEX
2	I	Arms Corporation	Philippines	JHP
3	A	Arms Corporation	Philippines	FMJ
	B	SME	Malaysia	FMJ
	E	Sellier and Bellot	Czech Republic	JHP
	H	Sellier and Bellot	Czech Republic	FMJ
4	J	Royal ammunition Co.	Thailand	JHP
	K	Remington Arms	United States	JHP
5	C	Inceptor-Polycase	United States	ARX
	G	Bullet Master Co.	Thailand	LRN

In short, the OGSR profiles might not related to make up of ammunition, probably based on the preference and desired performance of the manufacturers. The comparison had revealed a lack of discernible linkages among the tested samples, reaffirming the distinctiveness of each category. However, the application of proposed screening methodology was found useful in differentiating the various types of ammunitions, in this case, organic GSR profiles from the eleven tested spent cartridge cases. Inclusion of greater number of GSR profiles in future studies could provide a more thorough comparison for forensic investigation and intelligence. The flow chart-based approach to screen the OGSR profiles could emerge as a potent tool in forensic investigations.

From the findings of this study, SPME demonstrated its potential to be applied for the detection of OGSR from spent cartridge cases. Its simplicity and requirement of minimal sample preparation procedure could reduce the risk of sample contamination. Allowing for preservation of original spent cartridge case samples also provide the opportunity for subsequent analyses by any complementary techniques or re-evaluation of the same sample if required. As this study only restricted to qualitative detection of organic compounds present in the GSR, the SPME shall be further explored for quantitative study by considering the detection limits of each target substance and determination of their concentration levels in the cartridge case samples. Experimental outcomes by SPME shall also be compared to the conventional solvent extraction technique for maximum recoveries, especially for the trave-level GSR. In addition to that, comparison of the profiles of smokeless powder before firing and the post-firing GSR is also recommended in future study to investigate their profile changes upon firing.

Conclusion

This research was conducted to profile the OGSR extracted from spent cartridge cases by SPME-GC-MS. Among the detected OGSR compounds, significant findings included the presence of DPA, DBP, EC, butyl citrate and TAC. A comparative assessment of OGSR profiles across different ammunition types revealed the detection of stabilisers and plasticisers. DBP emerged as the most prevalent OGSR compound, being present in all the eleven tested samples. In contrast, butyl citrate was the least frequently observed compound, detected in just one sample. Lastly, the proposed screening methodology revolved the assessment for the presence or absence of specific compounds in each sample, allowing for the categorisation of unknown samples with respect to potential ammunition types or differentiated from specific sources. The eleven tested samples were successfully divided into five different groups based on their OGSR profiles. Such a strategy enabled a comparative analysis of OGSR profiles, thereby contributing to the forensic scrutiny of gunshot-related incidents.

Acknowledgements

Special thanks to the Royal Malaysia Police for their supply of ammunition samples.

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