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Q2 Preliminary classification of characteristic organic gunshot residue compounds

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ABSTRACT

For the first time, a classification system for organic gunshot residue (OGSR) compounds with respect to the confirmation of OGSR materials is presented. There are 136 compounds considered to be associated with OGSR that have been highlighted in the literature. Many of these compounds could be classified as being ubiquitous in the environment and thus their detection as characteristic components of OGSR could cause issues with the interpretation of chemical ballistic evidence. The proposed system aims to address this problem by classifying OGSR compounds based on their forensic relevance with respect to the confirmation of GSR materials. To increase the forensic relevance of such a system, the large number of OGSR compounds reported in the literature has been decreased to 20 OGSR compounds based on the organic chemical composition of over 200 propellant powders. Occupational and environmental materials also associated with OGSR compounds have been considered.

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1. Introduction

Gunshot residue (GSR), which is also known as cartridge discharge residue (CDR) or firearm discharge residue (FDR) [1], escapes from weapon openings [2] and may subsequently deposit on surfaces in the near vicinity of the fired weapon [3]. GSR can, therefore, be used as (trace) evidence consequent to the criminal use of firearms. Its use to establish a link, however, between the shooter, the firearm, the victim and/or the crime scene requires careful interpretation of the evidential value of GSR materials [4]. Unfortunately, due to the complexity of the firing process and the large number of parameters involved in the creation of GSR, both the amount and composition of GSR vary. Further diversity is promoted by the wide range of firearms and ammunition available [3].

Currently, for the detection and confirmation of GSR materials, scanning electron microscopy (SEM) techniques are employed for forensic work [1–4]. These methods are well established and guidelines by the ASTM [5] and forensic science working groups (e.g. SWGGSR [6]) provide definitive information on the classification and characterisation of inorganic particles (both morphology and metallic composition). The classification indicates if particles are deemed as being characteristic (i.e. most likely associated with the discharge of a gun), or consistent (i.e. may be associated with GSR). Such particle classifications take into account contamination from environmental sources (e.g. lead

particles). Equivalent information for organic GSR (OGSR) compounds is currently more ambiguous.

Due to the introduction of ‘lead-free’ or ‘non-toxic’ ammunition developed for health and environmental reasons [7,8], the unambiguous confirmation of GSR materials according to the current standards [5] is challenged [7–10]. This calls for an approach based on other compounds than the traditional metallic residues, to further strengthen the evidential value of GSR evidence. A potential alternative could be the determination of OGSR compounds [7–10].

There appears to have been a resurgence of interest in the analysis and detection of OGSR materials in recent years [9,11–13]. A comprehensive review by Goudsmits et al. [14] discusses recent developments in both extraction and analytical methods employed, and also highlights 136 compounds that have a possible association with OGSR. Many of these compounds, however, can be found in environmental and occupational materials [2,14], thus raising the question of their detection as being useful and relevant in regards to the interpretation of forensic evidence. It is currently unclear which compounds could be considered to be truly characteristic OGSR materials.

The aim of this paper is to facilitate a move towards the effective inclusion of OGSR compounds with respect to the confirmation of GSR materials. A first step is made in the form of a proposed classification system organising the compounds with the most forensic relevance into three different categories.

2. ‘Characteristic OGSR’

The term ‘characteristic’ is not new to OGSR materials. Mach et al. (1978) [15] classified respectively ethyl centralite (EC), 2,4-dinitrotoluene

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(2,4-DNT) and diphenylamine (DPA) as the three most characteristic OGSR compounds. Nitroglycerin (NG), 2,4-DNT, DPA, and some of its nitrated derivatives have been reported to be characteristic for the confirmation of GSRs using micellar electrokinetic capillary electrophoresis (MECE) [16]. The first classification suggests that the term characteristic is independent of the analytical methodology used for the detection of the compounds, whilst the instrumental technique is included in the latter definition. In addition, it is not outlined whether the single compounds or the combination of compounds are classed as characteristic for the confirmation of GSR *via* its organic constituents. Both points illustrate that there is no consensus on a clear definition of characteristic yet. Furthermore, criteria for the selection of characteristic OGSR compounds are not evident to date.

The confirmation of GSR materials based on inorganic compounds currently relies on particle analysis, *i.e.* the evaluation of constituent elements within a particle [5]. This approach is mostly not applicable to analysis of organic compounds due to the nature of the analytical techniques used, *e.g.* chromatography [8,9,12,17] and ion mobility spectrometry [13,18]. OGSR compounds are detected using so called bulk sample methods [5], in which a degree of correlation between the detected compounds is lost, *e.g.* the individual compounds could potentially originate from different, unrelated sources. This stresses the importance of a careful selection and evaluation of characteristic compounds.

Consequently, in order to set up a clear and reliable classification system for OGSR compounds it is imperative to define terms as 'characteristic' and to define transparent selection criteria. Furthermore, it is important to define the boundaries of characteristic OGSR, more specifically in relation to the weight of evidence that may be attributed to them in the court of law. For instance, Benito et al. [8] stated that "detecting degradation products of DPA and centralites is evidence of having shot a firearm or being in the proximity of a firearm discharge". In this communication a more careful interpretation of characteristic is adopted.

2.1. Defining 'characteristic OGSR'

Due to the generic use of bulk sample methods in the analysis of OGSR compounds to date, the authors suggest that for the confirmation of GSR materials *via* its organic constituents a combination of compounds should be detected. Consequently, 'characteristic OGSR' is defined as a combination of organic compounds associated with gunshot residue, which are not generally found in the (occupational) environment.

This definition recognises the current standard for the confirmation of GSR materials. This paper does not aim to preplace the current standard, but merely to facilitate a move towards the inclusion of OGSR compounds as complementary evidence.

If the proposed system may evolve to a stand-alone classification system for OGSR compounds, it may be used for the confirmation of GSR materials using or based on OGSR compounds. Similar to the current ASTM guidelines [5] the detection of what is defined as characteristic OGSR does not imply the guilt of a suspect by default, but merely the presence of OGSR materials. The (weight of the) evidence always needs to be evaluated in the context of the case.

2.2. Selection criteria OGSR compounds

Extracting as much information as possible from GSR samples would increase the value of GSR evidence [14]. Many organic compounds currently associated with GSR, however, have limited forensic relevance with respect to the confirmation of GSR materials. The forensic relevance of individual compounds is imperative due to the loss of correlation between compounds, resulting from the bulk sample analysis rather than particle analysis. In order to re-establish a correlation between the detected compounds and GSR materials it is of primary

importance that the compounds considered have a known origin, and that only identified compounds will be considered.

The main sources for OGSR compounds are ammunition components (*e.g.* propellant powder), and (combustion) products produced during the discharge of a firearm [14]. Due to the complexity of the firing process the composition of GSR may vary [3], and as a result the compounds created during the discharge of a firearm are not necessarily reproducible. Furthermore, many of these compounds, such as naphthalene and other polycyclic aromatic hydrocarbons (PAHs), although present in OGSR materials, are also universal combustion products [19–21]. Consequently, in this light these compounds do not satisfy the criteria of a known origin. Detection of OGSR compounds from ammunition components, such as propellant powder or primer mix, however, can provide consistent and repeatable results.

The forensic relevance of compounds further depends on the strength of the association with GSR materials (*e.g.* are the compounds frequently detected in ammunition components, or only sporadically?), and the significance of the detection of the compounds (*e.g.* do the compounds have a limited or widespread occupational and/or environmental prevalence?).

In summary, the criteria that need to be considered in the selection of suitable compounds that could potentially provide complementary evidence with respect to the confirmation of OGSR materials are:

- compounds should have a known origin (*e.g.* ammunition components);
- compounds should have a strong association with the ammunition components;
- compounds should have a limited occupational and environmental prevalence.

3. Characterisation of ammunition components

OGSR compounds predominately originate from the propellant powder [22]. Modern, smokeless powders are based around nitrocellulose (NC) as an explosive (single base powders); a combination of NC and nitroglycerin (NG) (double base powders); or a combination of NC, NG and nitroguanidine (NQ) (triple base powders). In addition to these explosive compounds, all smokeless powders contain a number of additives including stabilisers, sensitisers, plasticisers, flash inhibitors, coolants, moderators, surface lubricants, and anti-wear additives [22]. Some of these compounds, mainly explosive compounds and sensitisers, may originate from the primer mix [2,14].

A 136 organic compounds are currently associated with OGSR [14], many of which are linked to ammunition components [2]. In order to investigate which OGSR compounds could potentially provide complementary evidence with respect to the confirmation of GSR materials the organic compositions of over 200 propellant powders reported in the literature have been evaluated. This data analysis has resulted in a short list of 20 compounds (Table 1) that abide the first two selection criteria, and therefore may be promising compounds for OGSR classification.

4. Occupational and environmental occurrence of OGSR compounds

Evaluating the potential of compounds to provide complementary evidence with respect to the confirmation of the presence of OGSR materials requires accurate information on their occurrence in the daily and occupational environment [26]. Centralites rarely exist in the normal environment [27] and their use is reportedly restricted to ammunition [8]. Ethyl centralite as well as akardite II are additives in (double-base) propellant powders for rockets [22,26], but no other data on the occurrence in the daily environment was found [26]. Nitroglycerin and nitrocellulose are both used in pharmaceutical preparations [26,27]. Nitrocellulose also occurs in lacquers, varnishes and celluloid films [26,27] and in printing [26]. The only other application

t1.1 **Table 1**
t1.2 **Q1** Characterisation of propellant powders and spent cases.

t1.3	Reference	[23]	Unpublished data ¹	[9]	[17]	[18]	[12]	[7]	[15]	[24]	[16]	[25]	
t1.4	Type of sample	Spent cases		Propellant powder									
t1.5	Number of samples	n = 2	n = 2	n = 6	n = 4	n = 13	n = 65	n = 9	n = 5	n = 33	n = 2	n = 106	n = 38
t1.6	2,4-Nitrodiphenylamine								2				
t1.7	2,4-Dinitrotoluene				3		~28		1	13	2	22	15**
t1.8	2,6-Dinitrotoluene										1	6	
t1.9	2-Nitrodiphenylamine	2		5		10	~33	2	1		2	38	
t1.10	4-Nitrodiphenylamine	2		5	2	9	~24		2		2	38	
t1.11	Dibutylphthalate	2		2	2	4				12		35	10
t1.12	Diethylphthalate												
t1.13	Diphenylamine	2	1	5	3	12	62	8	5	27	1	71	32
t1.14	Ethyl centralite	2	2	5	2	10	~31	5	4*	11	1	54	8
t1.15	Ethylphenylamine		1				1						
t1.16	Methyl cellulose								1				
t1.17	Methyl centralite		1	1			~5		4*			2	5
t1.18	Nitroglycerin	2		4	3	10		8		27	1	89	22
t1.19	N-Nitrosodiphenylamine					9			2		1	75	
t1.20	Akardite II			2				2					
t1.21	Triacetin		1										
t1.22	Carbazole	1		1									
t1.23	3-Nitrotoluene					2							
t1.24	4,4-Dinitrodiphenylamine	2											
t1.25	2,4,6-Trinitrotoluene								1		1		

t1.26 ~Approximate numbers were interpolated from a diagram, exact numbers were not included in the paper.

t1.27 * Method used could not distinguish between EC and MC, hence it is unknown which centralite is present.

t1.28 ** Dinitrotoluene isomers (2,3-DNT, 2,4-DNT, 2,6-DNT, 3,4-DNT) were grouped together.

t1.29 ¹ Goudsmits, E.; Sharples, G.P.; Birkett, J.W. (2015), unpublished experimental data.

of 2,4-dinitrotoluene found is the presence in several azo dyes [28]. Diphenylamine is predominantly used as a stabiliser in NC containing explosives and propellants [28]. It is most commonly present in GSR samples [29] and in propellant powders as shown in Table 1, often as one of the highest peaks [13]. It must be noted, however, that DPA is a compound from the third European Union list of priority pollutants [28] and has wide applications. It is used in rubber products, the food industry, dyes, explosives, plastics, pharmaceuticals, the agricultural sector (on apples and pears, to prevent post-harvest deterioration), perfumery, elastomer industry and in photography chemicals [26–28]. DPA is found in soil and groundwater, and it occurs naturally in onions, leaves of black and green tea, further plants and the peel of citrus fruits [28]. On the other hand, reports on non-GSR-related contamination are inconsistent; contamination has been observed [22], but no mention of false positives due to DPA contamination has been made in several studies [13,26,30]. It is known that DPA reacts with nitric and nitrous acids that result from the degradation of NG and NC, transforming DPA into its mono-, di-, and tri-nitrated-derivatives [8]. These derivatives have been reported to be characteristic to smokeless powders [8]. Consequently, despite the presence of DPA on its own not being significant due to its wide applications, relevance may be attached to its presence in conjunction with its nitrated-derivatives [22,26]. 2-Nitrodiphenylamine and 4-nitrodiphenylamine are added to smokeless powders as stabilisers as well [18]. Other applications of 2-NDPA include its use in several azo dyes and in US Navy fuel for torpedoes and other weapon systems [28]. 4-NDPA may also be a compound in azo dyes, and it is an intermediate for the production of antioxidant additives for rubber products [28]. Of the phthalates particularly dibutylphthalate is frequently associated with OGSR materials. Phthalates are, however, ubiquitous to indoor air, settled dust and food. This is due to their wide application as plasticisers in a broad array of polymeric materials and the fact that phthalates are not chemically bonded to the materials. Consequently, they are susceptible to leaching and are, therefore, readily released into the environment [31]. Apart from being universal combustion products, PAHs are in general persistent and ubiquitous environmental pollutants [19–21].

Due to the wide prevalence of phthalates and PAHs, these compounds are unsuitable for the confirmation of GSR materials.

They may be used, however, to differentiate between different propellant powders or GSR samples, or for time since discharge studies [11,23].

4.1. Population studies

The authors recognise that the data on the occurrence of OGSR compounds in the environment is incomplete without a thorough population study, in which data is obtained on the actual prevalence of these compounds in the environment. Some population studies with respect to the prevalence of explosive compounds have been performed [32–34]. A few of these compounds are also relevant to GSR materials, namely NG, trinitrotoluene (TNT) and (di)nitrotoluenes including 2,4-DNT.

Samples in these population studies were taken from locations such as airports, vehicles, and government and public buildings. None of these compounds were found in 333 samples collected throughout the United States [32], or in 255 samples taken in and around London [33]. Of the 493 samples taken from Manchester, Birmingham, Glasgow and Cardiff, only two were positive for nanogram levels of NG (Glasgow taxi floor and a wardrobe in a hotel in Cardiff), and only one sample was positive for nanogram levels of 2,4-DNT (the back of an X-ray machine in the search area at Glasgow Airport) [34]. From 255 samples collected from police vehicles and police custody suits in and around London only 15 samples were positive for nanogram levels of NG [33].

With respect to OGSR compounds, a study has been performed sampling the hands of 100 individuals from the general population. OGSR compounds studied included NG, DNT's including 2,4-DNT, DPA and some of its nitrated derivatives, centralites and phthalates. Despite detection limits in the picogram range no OGSR compounds were detected [35].

Due to the fact that in this paper the large number of OGSR compounds currently associated with GSR will be narrowed down significantly to a smaller group of compounds with an increased forensic relevance, this could potentially provide the basis for such a population study on OGSR compounds. The obtained data could then be used to optimise the proposed selection of OGSR compounds.

5. OGSR as complementary evidence

The analysis of the data has highlighted that many organic compounds currently associated with GSR have limited forensic relevance with respect to the confirmation of GSR materials. This could limit the effective use of OGSR as complementary evidence to IGSR information, whilst the confirmation of GSR materials via the inorganic constituents suffers from the introduction of 'lead-free' or 'non-toxic' ammunition. In these types of ammunition lead, barium and antimony in the primer mix may have been replaced by other compounds [7], complicating the unambiguous confirmation of GSR materials that is currently based on these compounds [5]. OGSR compounds could thus provide valuable, complementary information, and potentially provide additional means to discrimination between GSR materials and environmental residues [8,9].

A first step towards the effective inclusion of OGSR compounds to the confirmation of GSR materials is made in the form of a proposed classification system (Table 2). This system organises the compounds with the most forensic relevance into three different categories based on the formulated criteria (Section 2.2).

Category 1 contains the compounds with highest forensic relevance *i.e.* these compounds have a very strong association with OGSR and their detection is significant due to the very restricted applications that are unrelated to OGSR.

Category 2 contains compounds that are strongly associated with OGSR, based on analysis of the propellant powders (Table 1). The usage of these compounds, however, is less restricted and thus more applications unrelated to OGSR may exist. This reduces the significance of their detection due to their (potential) occupational and environmental prevalence.

Category 3 contains compounds to which the lesser restriction of usages, and thus a reduced significance of detection may also apply. In addition, although these compounds are associated with ammunition components (Table 1), they are detected less often and thus have a reduced association. Further OGSR compounds may be added to the proposed system if deemed necessary and if they meet the set criteria.

This system contains a few exceptions based on Table 1, due to the fact that the overall perceived forensic relevance is the leading factor for the categorisation, and not any one criteria by itself.

Despite being absent in Table 1 due to the lack of detection in published work, NC and NQ are included in the system, due to the fact that they are base compounds of propellant powder. NC is present in single, double and triple base powders. This high association cancels out the low experimental association based on Table 1. The lesser

restrictions of applications that are not related to OGSR warrants the inclusion of NC in category 3. NQ is only present in triple base powders, but it is included in Category 1 due to its very limited (reported) applications unrelated to GSR. The latter is the same reason for including akardite II to Category 2, despite its low experimental association.

Dibutylphthalate has a relatively high association to OGSR materials, however, due to the generic use of bulk sample analysis for its detection, its wide-spread prevalence excludes it from the proposed classification system. Similarly, DPA is only included in conjunction with its nitrated-derivatives due to its relatively high occupational/environmental prevalence.

With continual changes being made to ammunition composition, such a classification system will need to be kept under constant review to add or remove compounds based on analysis and manufacturer information.

It should be noted that the aim of this classification system is to highlight OGSR compounds with forensic relevance with respect to the confirmation of GSR materials, to potentially provide a backbone for a classification system including organic gunshot residue. Consequently, in the current forensic setting, this system may be used to complement inorganic GSR information; it is not suggested as a replacement of the existing standard.

5.1. Analytical techniques

The proposed classification system is independent of the analytical techniques employed for the detection of OGSR compounds, because the authors are of the opinion that at this stage it should be based solely on the compounds of interest, *i.e.* OGSR. Consequently, it may not be possible to target all of the OGSR compounds included in Table 2 in a single analysis. It is also possible that the concentration of some of compounds present in the ammunition components drops below the detection limit of the applied methodology post firing. The authors consider that this is not a reason to exclude compounds at this stage, but rather an incentive to optimise the sampling, extraction and analytical methodologies. This is due to the fact that there is currently an absence of a set combination of sample collection, extraction and analysis methods that is universally optimal for the treatment of any given OGSR sample [14]. The detection of complementary organic and inorganic GSR compounds from a single sample is especially challenging. Further improvements in the detection of OGSR compounds could continue to build on the proposed classification system.

Table 2
Classification system for OGSR compounds.

Category	Description	Compounds	Function
1	Compounds that are very strongly associated with GSRs with very restricted applications unrelated to GSR	Ethyl centralite Methyl centralite Nitroglycerin Nitroguanidine	Stabiliser Stabiliser Explosive Explosive
2	Compounds that are strongly associated with GSRs, but which have less restricted applications unrelated to GSR	2,4-Dinitrotoluene Akardite II 2-Nitrodiphenylamine 4-Nitrodiphenylamine Diphenylamine + nitrated-derivatives	Flash suppressor Stabiliser Stabiliser Stabiliser Stabiliser
3	Compounds that are associated with GSR, but which are detected less frequently and have less restricted applications unrelated to GSR	Nitrocellulose Other nitrotoluenes (2-NT, 3-NT, 4-NT, 2,3-DNT, 2,5-DNT, 2,6-DNT, 3,4-DNT, TNT) Other diphenylamine derivatives (Ethylphenylamine and 2,4-NDPA, N-NDPA <i>etc.</i>) Triacetin	Explosive Flash suppressor Sensitiser Stabilisers Plasticiser

6. Summary

There are 136 compounds considered to be associated with OGSR that have been highlighted in the literature. Many of these compounds could be classified as being ubiquitous in the environment, and thus their detection as a possible component of OGSR could cause issues with the interpretation of chemical ballistic evidence. The organic compositions of over 200 propellant powders reported in literature have been evaluated. This has resulted in a shortlist of 20 compounds that may be promising target compounds for the confirmation of GSR materials. A definition for characteristic OGSR compounds has been formulated, and a classification system describing characteristic OGSR compounds is proposed. The system is based on the shortlist, and divides compounds into three categories based on their forensic relevance with respect to the confirmation of GSR materials. This may enable a move towards the effective inclusion of OGSR compounds as complementary evidence. Ongoing work by the authors is currently implementing the proposed system to actual GSR samples.

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