Recent trends in organic gunshot residue analysis

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Highlights

- A list of 136 compounds associated with organic gunshot residue (OGSR) is presented
- Recent developments in methods for the extraction and detection of OGSR are highlighted
- Analytical techniques aiming to provide a full chemical profile are discussed
- It is concluded that the optimal methodology for any OGSR sample should be based on a 'case-by-case' approach

Abstract
A comprehensive review of the literature concerning all aspects of sampling and analytical techniques used for the determination of organic gunshot residue (OGSR) compounds is presented. Currently, 136 compounds associated with OGSR have been identified in the literature. Despite this area gaining increasing attention and recognition in recent years, there is still an absence of a set combination of sample collection, extraction and analysis methods that are universally optimal for the treatment of any given OGSR sample. Moreover, there are no generally accepted guidelines for selecting the compounds of interest that will inform sampling and analysis protocols. Recent developments in both extraction and analytical methods employed for their detection are highlighted. The main advantages and disadvantages of the sampling and analysis methods are critically discussed.

Keywords
Forensic science, ballistics, gunshot residue, organic gunshot residue, chromatography, solid phase micro extraction, ion mobility spectrometry, spectroscopic detection, electrochemical detection

Abbreviations
Techniques and parameters:
APCI: Atmospheric pressure chemical ionisation, ATR: Attenuated total reflectance, CE: Capillary electrophoresis, DESI: Desorption electrospray ionisation, DMA: Differential mobility analysis, ECD: Electron capture detection, EDX: Energy dispersive X-ray spectroscopy, ESI: Electrospray ionisation, FID: Flame ionisation detector, FTIR: Fourier transform infrared, GC: Gas chromatography, HPLC: High performance liquid chromatography, IMS: Ion mobility spectrometry, LC: Liquid chromatography, MECE: Micellar electrokinetic capillary electrophoresis, MEKC: Micellar electrokinetic capillary chromatography, MS: Mass spectrometry, MS-MS: Tandem mass spectrometry, PMDE: Pendant mercury drop electrode, QTOF: Quadrupole time of flight, SCF: Super critical fluid, SEM: Scanning electron microscopy, SIMS: Secondary ion mass spectrometry, SPE: Solid phase extraction, SPM: Solid phase micro extraction, TD: Thermal desorption, TEA: Thermal energy analysis, TLC: Thin layer chromatography, TOF: Time of flight, UPLC: Ultra performance liquid chromatography, UV: Ultra violet.
Compounds and chemicals:
AKI: Arkadite I, AKII: Arkadite II, AKIII: Arkadite III, BC: Butylphthalate, CAR: Carboxen, DBP: Dibutylphthalate, DEP: Diethylphthalate, DMP: Dimethylphthalate, DNAN: 2,4-Dinitroanisole, DNT: Dinitrotoluene, DPA: Diphenylamine, DVB: Divinylbenzene, EC: Ethyl centralite, GSR: Gunshot residue, HMX: Octogen, IGSR: Inorganic gunshot residue, MC: Methyl centralite, NC: Nitrocellulose, NDPA: Nitrodiphenylamine, NG: Nitroglycerin, OGSR: Organic gunshot residue, PA: Polyacrylate,
PAH: Poly aromatic hydrocarbons, PDMS: Polydimethylsiloxane, PETN: Pentaerythritol tetranitrate, RDX: Cyclonite, TNT: 2,4,6-Trinitrotoluene.

Contents

1. Introduction

Gunshot residue (GSR) is the collective name of the complex mixture of organic and inorganic particles [1] originating from the firearm, the firearm ammunition and the combustion products, which are produced during the discharge of a firearm [2]. GSR consists of unburnt and partially burnt particles. Compounds from ammunition primer, propellant powder and metals from the projectile arise from firearm ammunition. Grease, lubricants and metals from the gun barrel are contributed by the firearm [1-3]. Organic compounds mainly originate from propellant powders, firearm lubricants, some products of their transformation and hydrocarbons. Inorganic compounds, such as nitrates, nitrites and metallic particles, originate from the primer and propellant, as well as the cartridge case, projectile jacket and its core and from the gun barrel [1, 2].

Present analysis methods of GSR in forensic investigations mainly focus on inorganic GSR (IGSR) analysis using scanning electron microscopy (SEM) methodologies [1, 4]. Combining this information with organic GSR (OGSR) information, however, would significantly increase the probative value of GSR evidence [5], as it enables a more accurate interpretation of obtained analytical results [2]. This review discusses organic compounds which could be associated with smokeless powders and gunshot residue. Recent developments in both extraction and analytical methods employed for their detection are highlighted. A brief overview of key milestones in OGSR analysis is presented in figure 1.

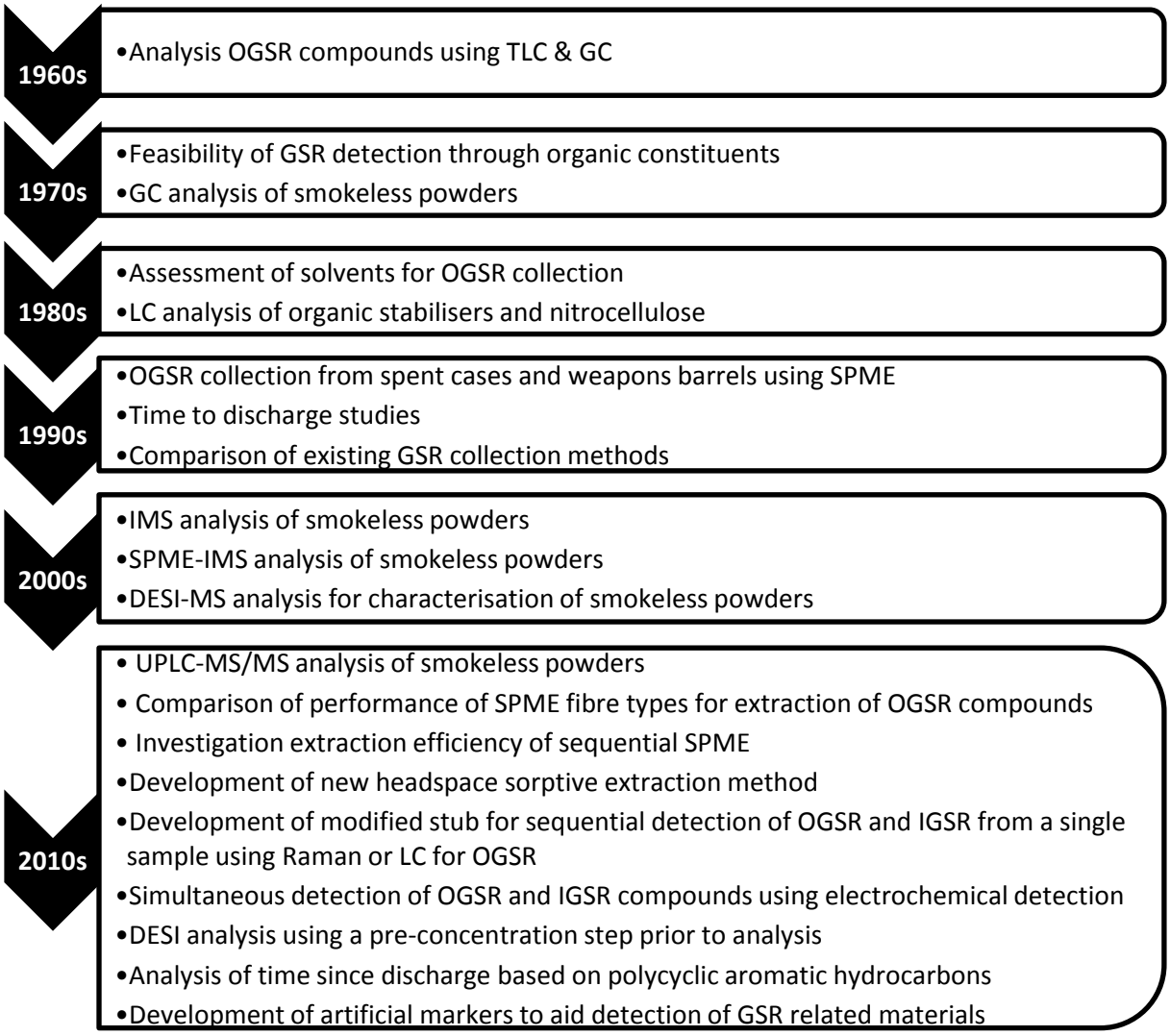

Figure 1: Key milestones in OGSR analysis

1.1 Organic GSR compounds

Dalby *et al.* [2] produced a comprehensive list of 48 organic compounds that may contribute to gunshot residue and their sources. This list is highlighted in a more recent review by O'Mahony and Wang [6]. This seemingly indicates a general consensus on possible organic compounds associated with smokeless powders and gunshot residue. A list of compounds provided by Taudte *et al.* [7] in 2014, concerning the organic compounds commonly used in the manufacturing of propellant powders and primers, contains approximately 60% of the compounds highlighted in the previous lists [2, 6]. The most noteworthy compound, which is absent from the list, is nitrocellulose. The new compounds predominately, include additional phthalates, nitrobenzenes and nitrates.

The compounds listed in the mentioned reviews by Dalby *et al.* [2] and Taudte *et al.* [7] are compared against several experimental studies on OGSR compounds in table 1. The majority of these studies have been reported since 2010 [2, 7-12]. A few studies, including one review [3], prior to 2010 have been included for the purpose of comparison [13-15]. This has resulted in a list containing 136 organic compounds that could be associated with smokeless powders and gunshot residue.

Table 1: Organic compounds which may contribute to gunshot residue

Compound	Ref. experimental	Ref. review	Compound	Ref. experimental	Ref. review
1,2,3-Trimethylbenzene	[13]		Carbanilide		[2, 3]
1,2,4-Trimethylbenzene	[13]		Carbazole	[8, 9, 13, 16]	[2, 3]
1,3,5-Trimethylbenzene	[13]		Charcoal		[2]
1,3,5-Trinitrobenzene	[16]	[7]	Chrysene	[9]	
1,3-Dinitrobenzene	[16]	[7]	m-Cresol	[8]	[2, 3, 7]
1,2-Dicyanobenzene	[9, 13]		o-Cresol	[8]	[2, 3, 7]
1,3-Dicyanobenzene	[9, 13]		p-Cresol	[8]	[2, 3, 7]
1,4-Dicyanobenzene	[9, 13]		Cyclonite (RDX)	[8, 12, 16]	[2, 3, 7]
1,2-Dinitroglycerin		[7]	Dextrin		[2]
1,3-Dinitroglycerin		[7]	Diamylphthalate		[7]
1,4-Dimethylnaphthalene	[9]		Diazodinitrophenol		[2]
2,6-Dimethylnaphthalene	[9]		Diazonitrophenol		[2, 7]
1-Methyl-3,3-diphenylurea	[9]		Dibutylphthalate (DBP)	[3, 8-11, 13-16]	[2, 7]
1-Methylnaphthalene	[9, 13]		Diethylene glycol dinitrate		[7]
2-Methylnaphthalene	[9, 13]		Diethylphthalate (DEP)	[8, 10-12, 15, 16]	[2, 3, 7]
1-Naphthalenecarbonitrile	[9]		Dimethylphthalate (DMP)	[8, 10-12, 15, 16]	[2, 3, 7]
2-Naphthalenecarbonitrile	[9]		Dimethylsebacate	[8]	[2, 3]
2,2'-Dinitrodiphenylamine	[16]		Dinitrocresol		[2]
2,4'-Dinitrodiphenylamine	[16]		Dinitro-ortho-cresol		[3, 7]
4,4'-Dinitrodiphenylamine	[16]		Diphenylamine (DPA)	[3, 8-16]	[2, 7]
2,3-Dimetyl-2,3-dinitrobutane	[8]		Ethyl centralite (EC)	[3, 8-16]	[2, 7]
2,3-Dinitrotoluene (2,3-DNT)	[8, 11, 14-16]	[2, 3, 7]	Ethylbenzene	[9]	
2,4-Dinitrotoluene (2,4-DNT)	[3, 8, 10-12, 14-16]	[2, 7]	Ethylene glycol dinitrate		[2, 7]
2,6-Dinitrotoluene (2,6-DNT)	[8, 10, 11, 14-16]	[3, 7]	Ethylphthalate		[2, 7]
3,4-Dinitrotoluene (3,4-DNT)	[8, 10, 11, 14]	[7]	Fluoranthene	[9]	
2,4,6-Trinitrotoluene (TNT)	[8, 12, 16]	[2, 3, 7]	Fluorene	[9, 13]	
2,4-Dinitroanisole (DNAN)	[12]		Gum arabic		[2]
2,4-Dinitrodiphenylamine	[8, 9, 11, 12, 16]	[2, 3, 7]	Gum tragacanth		[2]
4,4-Dinitrodiphenylamine	[11]	[7]	Hexylene glycol	[13]	
2-Amine-4,6-dinitrotoluene	[12, 16]	[7]	Indene	[9, 13]	
4-Amine-2,6-dinitrotoluene	[12, 16]	[7]	Indole	[9, 13]	
2-Ethyl-1-hexanol	[9, 13]		Isoquinoline	[9]	
2-Ethylhexanal	[13]		Karaya gum		[2]
2-Ethylnaphthalene	[9]		Methyl cellulose		[2]
2-Furaldehyde	[13]		Methyl centralite (MC)	[10, 11, 15, 16]	[2, 3, 7]
2-Naphthol	[11]		Monomethyl-phthalate	[8]	[2, 7]
2-Nitrobenzene	[16]		Naphthalene	[9, 13, 16]	
3-Nitrobenzene	[16]		N,N-diphenylformamide	[16]	
4-Nitrobenzene	[16]		Nitrobenzene	[16]	[7]

2-Nitrophenylamine (2-NDPA)	[3, 8-14, 16]	[2, 3, 7]	Nitrocellulose (NC)	[3]	[2]
4-Nitrodiphenylamine (4-NDPA)	[8-12, 16]	[2, 3, 7]	Nitroglycerin (NG)	[3, 8-11, 13-16]	[2, 7]
2-Nitrotoluene	[8, 11, 14, 16]	[2, 7]	Nitroguanidine	[8, 12, 14]	[2, 3, 7]
3-Nitrotoluene	[8, 11, 14, 16]	[2, 7]	N-nitrosodiphylamine (N-NDPA)	[3, 8-12, 14]	[2, 7]
4-Nitrotoluene	[8, 11, 14, 16]	[2, 7]	Nonanal	[13]	
3,5-Dinitroaniline	[16]		Octogen (HMX)	[12]	[7]
4-Methylbiphenyl	[9]		Pentaerythritol tetranitrate (PETN)	[12]	[2, 3, 7]
4-Nitrosodiphenylamine	11, 10	[7]	Phenanthrene	[9, 13]	
Acenaphthene	[9, 13]		Phenol	[13]	
Acenaphthylene	[9, 13]		Phytane	[13]	
Acetophenone	[9]		Picric acid	[14]	[2]
Akardite I (AKI)		[7]	Pyrene	[9, 13]	
Akardite II (AKII)		[2, 7]	Quinoline	[9, 13]	
Akardite III (AKIII)		[7]	Resorcinol	[8, 15]	[2, 3, 7]
Aniline	[13]		Rubber cement		[2]
Anthracene	[9, 13]		Sodium alginate		[2]
Benzaldehyde	[9, 13]		Starch		[2]
Benzene	[9]		Styrene	[9, 13]	
Benzo[a]pyrene	[9]		Tetracene		[2]
Benzo[b]thiophene	[9]		Tetryl	[8, 16]	[2, 7]
Benzonitrile	[9, 13]		Toluene	[9]	
Benzophenone	[9, 13]		m-Tolunitrile	[9, 13]	
Benzothiazole	[9]		o-Tolunitrile	[9, 13]	
Benzylnitrile	[9, 13]		p-Tolunitrile	[9, 13]	
Biphenyl	[9]		Triacetin	[8]	[2, 3, 7]
Biphenylene	[9, 13]		Urethane	[8]	
Butylcentralite (BC)		[2, 3, 7]	m-Xylene	[9]	
Butylphthalate		[2]	o-Xylene	[9]	
Camphor	[8]	[2, 7]	p-Xylene	[9]	

Table 1 clearly shows that approximately half of the compounds, which have been of interest in the experimental studies, are not included in any of the mentioned reviews. Polycyclic aromatic hydrocarbons (PAHs), such as naphthalene - related compounds, benzo[a]pyrene and chrysene have been reported as constituents of OGSR. Despite this fact there is limited information in the literature regarding the analysis of PAHs in GSR [9, 13].

PAHs are widely spread, persistent and ubiquitous environmental pollutants [17-19], which can exist in both vapour and particle phases in the atmosphere [17]. They are present in vehicular emissions, tobacco smoke and industrial effluent [17-19]. PAHs are universal combustion products and are predominately formed during the incomplete combustion of organic matter such as wood, fuel, gas and coal [18, 19].

Due to the generic nature of PAHs, one could argue that the evidential value of these compounds with respect to the analysis of organic gunshot residue is very limited. It must be noted, however, that the specific studies including these compounds [9, 13] did not aim for the identification of gunshot residue based on these compounds, nor claim that these compounds are characteristic for OGSR. The purpose of both studies was to investigate the time since discharge. Gallidabino *et al.* [9] found PAHs particularly suitable for this purpose, since these substances are simultaneously produced during the discharge and are subjected to the same variability-introducing factors. It was expected that as a consequence of this, the PAHs present closer mutual fluctuations and thus could be used for the normalisation of the determined aging curve.

Primers can also be a source for OGSR [3]. More specifically, Meng and Caddy [3] referred to sensitising materials used in small-arm primers, such as tetracene, pentaerythritol tetranitrate (PETN), trinitrotoluene and tetryl. Additionally, the primer mix may also be a source for nitrocellulose (NC) and nitroglycerin (NG) [2]. All of these compounds are included in table 1, although these compounds may also originate from propellant powders [2]. The table does contain a few compounds that have been listed as primer mix compounds only in a review by Dalby *et al.* [2]. These compounds are dextrin, diazodinitrophenol, diazonitrophenol, gum arabic, gum tragacanth,

karaya gum, rubber cement and sodium alginate. Diazodinitrophenol is commonly mentioned as a non-toxic replacement for lead compounds in primers but was already included in patents since the early 1980s, often in conjunction with tetracene [20, 21]. There are, however, numerous patents for primers that include single or multiple other organic compounds, which are not included in the table and are not listed as propellant powder components. The patents are both recent, e.g. since the increase in lead free, non-toxic primers; and earlier, e.g. 1980s and 1990s [22]. The organic compounds listed in the primer-related patents include styphic acid, tetrazene, polynitrophenylether, polynitropolyphenylene, polyvinyl acetate, hexogene, actogene and nitropentene [23]. Furthermore, a patent published in 2013 describes a primer composition comprising of red phosphorus stabilized by an acid scavenger and a polymer, which gives rise to a whole new category of organic compounds [24].

1.2 GSR markers

Another area of approach to the identification of GSR is the development of artificial markers which could be added to ammunition in order to create a characteristic marker for GSR. These may be luminescent markers which consist of a metallic-organic complex [25-27], the chemical composition of which is by design not commonly found in the environment or in occupational tasks [25]. Such markers could considerably simplify investigative routines by enabling the visual detection and identification of GSR at the crime scene with the aid of an ultraviolet light source [25]. Additionally, by using different tags, the markers can be used to differentiate, for example, between ammunition for civil, law enforcement or military use [28].

A suitable marker should be thermally stable, chemically inert, have a high luminescence [26], not interfere with the ammunition's performance [29] and be of low cost [25]. Lanthanide-organic compounds meet all these criteria and are thus suitable as markers [28]. In an evaluation of the performance of these markers, it was found that they remain luminescent for up to 30 months, persist on hands for about 9 hours and are only removed after 16 hand washings. It was also found that markers which were deposited on the hands post-firing could be transferred to other objects. The authors suggested that this opens new perspectives for forensic analysis by increasing the diversity of sampling [29]. It must be noted, however, that the possibilities of further transfer from contaminated objects onto a third party and the possible implications of this, have not been investigated. Furthermore, the fact that these markers remain luminescent for 30 months may give rise to difficulties in the interpretation because these markers will potentially contaminate more areas and objects. This would diminish the suitability and evidential value of these markers. Moreover, if the use of markers became common, this would severely hamper the linkage of marker traces found at a scene to a specific incident. Another possible issue with the evidential value is the potential for marker compounds to be released during a discharge of unmarked ammunition following the firing of marked ammunition with the same gun. This could also be an issue when ammunition marked with different tags is fired with the same firearm. Investigation of these issues has not been reported. Additionally, detailed investigation of the toxicity of these metallic-organic markers has not been performed. Another major factor, on which the successful implementation of such markers hinges, is whether manufacturers will actually add these markers to their ammunition. Despite the fact that these markers are reported to be inexpensive, without legislation that calls for the inclusion of markers in ammunition, it is questionable whether manufacturers will add the artificial markers to their products. This research shows potential as a detection/screening procedure for the presence of GSR related materials, but is currently in its infancy.

Such approaches to the identification of OGSR, in conjunction with the different set of compounds of interest when investigating time since discharge and the lack of differences in compounds of interest with older studies, suggests that the question of which compounds make for good, reliable OGSR characteristics depends on both the aim of the study as well as on the intended analytical technique, rather than on new insights over time.

2. Sampling and analysis methods

In order to enable the analysis of OGSR compounds, an efficient collection method is required. The fact that GSR can be deposited on a wide variety of surfaces in the near vicinity of the fired weapon following discharge increases the importance of selecting the most appropriate collection method [2].

2.1 Collection and extraction of OGSR compounds

Surfaces which may be exposed to GSR include the scene of the incident, which may be a mobile location such as the interior and/or exterior of a vehicle. GSR may also be collected from skin, hair, or clothes of people, who can be either a shooter, a victim or a bystander [2, 30-33]. Different collection methods employed for these types of surfaces have been discussed previously [2, 3, 30]. A summary of these methods is given in table 2.

Swabbing is reported as the most common technique employed for the collection of OGSR from hands [3, 4]. The swabbing method requires the choice of a suitable solvent for the collection of GSR materials. Ethanol and isopropanol are mentioned as the best performing solvents [2, 34, 35]. Organic solvents are commonly used for the collection of explosives and associated materials. A drawback of the use of this type of solvent is the fact that it will dissolve many other compounds as well, causing interference issues [2]. In a study by Thompson *et al.* [36] water followed by Solid Phase Extraction (SPE) was shown to be effective for the recovery of organic explosive residues and provided much greater selectivity in most cases. A combination of water and isopropanol in combination with SPE was employed by Lloyd and King [37] for both explosives and firearms residue. In their study, SPE was performed in the container in which the swab was returned to the laboratory. They reported that the employed extraction procedure extracted the organic residue, whilst the inorganic residue remained on the swab. This allowed for a subsequent extraction of the inorganic residue by sonication in an organic solvent, followed by membrane filtration. Consequently, the organic and inorganic fractions could be separated prior to analysis.

Dalby *et al.* [2] reported that tape lifts are the most common procedure for the collection of inorganic residues from skin surfaces. A drawback reported on the use of carbon coated adhesives is a significant reduction in the recoveries of OGSR compounds after solvent extraction [38]. This challenge could be addressed by a novel approach to the tape lift method, which involves covering half of the carbon coated stub with parafilm and PTFE tape. This enables the simultaneous analysis of the carbon coated half for IGSR by SEM and the OGSR analysis of the uncoated, PTFE tape half of the stub [12]. Benito *et al.* [12] compared this method with swabbing by spiking the swab and stub with a standard solution that was allowed to evaporate. Both spiked media were dissolved in 1 mL of methanol and the OGSR particles were subsequently extracted using the same method. The reported results showed that the recovery of the modified stub was similar or better for the majority of the 17 compounds included in the standard mix. Lower recoveries were only obtained for dimethylphthalate, trinitrotoluene (TNT) and 2-nitrodiphenylamine.

An additional GSR collection method is the use of an adhesive film which can be pressed against the whole of the surface to be sampled. The method is aimed at the use on the skin of people who suffered firearms injuries but can also be used on other surfaces, such as leather. The main advantage of this method is that it can be used for the investigation of the shooting distance [39]. This method could solve the problem of accumulation of debris and thereby loss of stickiness, which may be observed when using the tape lift method [2], because the film is applied once to a surface, rather than repeatedly dabbed onto it. Although this method is suitable for colour testing and determination of the shooting distance [39], the increased surface onto which the analytes are collected is disadvantageous for analytical techniques aimed at the identification of compounds [40]. Since this method does not appear to be advantageous over traditional techniques with respect to the sampling of hands, the practical applications of this technique seem to be limited.

Table 2: Collection techniques for deposited GSR

Technique	Medium	Surface	Advantages	Disadvantages	Ref
Tape lifting	Stub with adhesive: - Carbon coated - Double sided tape	- Skin - Hair - Fabric	- Most effective - IGSR & OGSR - Cheap - Good collection efficiency - SEM compatible - Surface sampling only	- Build-up of debris - carbon or gold coating needed after sampling of fabric - Varying reports on suitability of hair sampling (200-300 dabs needed) - Loss of stickiness due to fibres and debris	[2] [4] [30] [34] [41] [42]
Swabbing	Cotton swab soaked in organic or aqueous solvent	- Hands - Face	- IGSR & OGSR - Aqueous solvents best - IGSR and OGSR separately extracted	- Less effective - Organic solvents require SPE - Separate extraction requires SPE	[2] [4] [30] [34] [37]
Combing	Fine tooth comb	Hair	- Particles smaller than gaps between comb teeth collected - Nearly intact grains collected	- Difficult with curly hair	[2] [43]
Swabbing & combing	(Fine tooth) comb with solvent swabs or a damp cloth between the teeth	Hair		- More complicated	[2] [44] [42]
Vacuum lifting	Vacuum with Teflon or fibre glass filter	Clothes	- IGSR & OGSR	- Combination with tape lifting (for OGSR) - Extraction needed - Sampling depth of fabric rather than surface only	[2] [4] [45]
Glue lifting	Glue lifting planchet (less sticky than tape)	Hands	- Less dabs than tape lift method - Less debris than tape lift method, - Thus faster SEM - Surface sampling only	- May be ineffective for particle lifting due to lesser tackiness than tape lifts	[2] [40]
Film lifting	Adhesive film cut to size to enable covering whole area at once	- Injured (facial) skin	- Only 1 ‘dab’ - Less debris than tape and glue lift method -Suitable for shooting distance investigation	- Large surface area hinders analysis	[39] [40]

Volatile OGSR compounds can be collected from human nasal tissue [2, 4], but more often it is associated with the collection of volatile compounds from spent cartridge cases and firearm barrels. The collection of OGSR compounds from cartridge cases generally involves the collection of the case itself in an airtight container [9, 13], or seal bag [46], followed by extraction in a laboratory. The use of solid phase micro extraction (SPME) is generally the method of choice for the collection of volatile OGSR compounds from the barrel of a firearm [47-49].

2.1.1 Solid phase micro extraction

SPME is a solvent-free variety of solid phase extraction (SPE) and employs a fine fused silica fibre coated with a polymeric substance, the sorbent phase, to extract volatile organic compounds from their matrix [47]. The principle of the extraction is based on the partition equilibrium of analytes between the matrix and the sorbent phase [9]. This technique allows the collection of (ultra-)trace levels of analytes from liquid, gaseous and solid samples, due to the fact that the analytes are concentrated onto the fibre [8]. SPME has wide applications within different analytical fields because of its simplicity, efficiency and good precision. With respect to OGSR analysis, SPME is applied to the identification of OGSR compounds from spent cartridges [8, 50] and smokeless (propellant) powders [8]; and to the determination of time since discharge from cartridge cases [9, 13], as well as gun barrels [47]. The latter application is a specific advantage of the suitability of SPME to the sampling of narrow spaces, like firearm barrels [47]. The major advantage of this technique, however, is the fact that thermal desorption of the SPME fibre enables the direct transfer of the analytes into the injector of a gas chromatograph (GC) [47], eliminating the need for additional extraction steps.

Different parameters, which may be considered when selecting the appropriate SPME method, are the fibre type, the sampling time and temperature and the desorption temperature There are several different types of SPME fibres, which vary in both the type and the amount of sorbent phase. Fibres may be coated with a single polymeric substance such as polydimethylsiloxane (PDMS) or polyacrylate (PA), or with a combination of polymers such as PDMS/divinylbenzene (PDMS/DVB), carboxen/PDMS (CAR/PDMS) or DVB/CAR/PDMS [8, 9, 13, 16, 47, 50, 51]. The PDMS only fibres are non-polar, the PA fibres are polar and the combined coatings are bipolar [8]. The performance of all of these fibre types in the detection of 32 OGSR compounds has been previously evaluated [8], including various quantities of PDMS sorbent in the single coated fibres. It was reported that PDMS/DVB was the most suitable fibre type for the extraction of OGSR compounds across the investigated ammunition types. A comparison between different, albeit less, fibre types – not including the PDMS/DVB fibre - has also been made in several other studies which focussed on the extraction efficiency of sequential SPME [51] and on the determination of time since discharge [9, 13]. The fibre types investigated are shown in table 3. The best performing fibre types are indicated in bold type. The two studies investigating the time since discharge [9, 13] included a significant amount of PAHs as indicated in table 1. This may affect the performance and thereby the suitability of individual fibre types, as it was reported that the performance of a fibre type may differ between different propellant powders [8]. This indicates that both the type of sample and the compounds of interest are variables, which need to be considered when selecting an SPME fibre.

Table 3: SPME parameters used in OGSR analysis

Fibre type	Extraction Time	Extraction Temperature	Desorption Temperature	Ref
7µm PDMS	35 min	40°C	250°C	[8]
30µm PDMS				
100µm PDMS				
85µm PA				
65µm PDMS/DVB				
85µm CAR/PDMS				

50/30µm DVB/CAR/PDMS				
85µm PA	40 min	80°C	280°C	[9]
85µm PA 100µ PDMS 75µm CAR/PDMS	40 min	Room T	280°C	[13]
100µm PDMS	5 min	Room T	250°C	[50]
85µm PA 100µm PDMS 7µm PDMS	21 min	66°C	250°C	[51]
85µm PA	30 min	Room T	170°C & 200°C	[47]
85µm PA 100µm PDMS 7µm PDMS	60 min	30°C	250°C	[16]

A number of the studies have also investigated the optimal sampling/extraction time. Dalby and Birkett [8] compared time periods between 5 min and 55 min, at 10 min increments, using a PDMS/DVB fibre. They determined that an extraction time of 35 min was suitable. Weyermann *et al.* [13] found a similar extraction time of 40 min adequate when using a PA fibre and comparing five extraction times between 20 min and 70 min. Joshi *et al.* [50], however, selected an extraction time of 5 min from a range of six times between 1 min and 60 min; reporting that the 100µm PDMS fibre was able to extract sufficient amounts of various compounds of interest at this short extraction time. It must be noted that this study only included eight compounds and thus this short extraction time may be insufficient when including a greater number of compounds, as has been the case in the other two studies [8, 13].

A consensus as to the optimal extraction temperature required for SPME-OGSR analysis has not been found. Temperatures ranging from room temperature [13, 47, 50] to 80°C [9] have been reported, usually without reporting the basis on which the temperatures were chosen. Two exceptions are the studies by Dalby and Birkett [8] and the study by Weyermann *et al.* [13]. Dalby and Birkett selected a temperature of 40°C as this temperature is high enough to volatilise the compounds of interest in the headspace of the vial but too low to cause thermal degradation of nitroglycerin, which is known to start at temperatures above 50°C [52]. Weyermann *et al.* compared room temperature extraction with an extraction temperature of 80°C to study the influence of temperature. It was reported that the increased temperature caused lower concentrations of some compounds, such as benzonitrile and naphthalene, but higher concentrations of compounds such as diphenylamine, fluorathene and pyrene. They also detected several additional compounds at higher temperatures, whilst other compounds resulted in unidentified spectra. They concluded that the higher temperature was undesired for their study because they felt the higher temperatures provoked diminution of signals related to some compounds of interest and made it impossible to perform a second analysis of the cartridges [13]. In the study by Gallidabino, however, which was also aimed at the investigation of time since discharge, 80°C was selected as the extraction temperature [9]. Both studies included a significant amount of PAHs. Despite the fact that over half of the investigated OGSR compounds were included in both studies, there was still a substantial number of selected PAHs which varied between the two (see table 1). Moreover, despite using the same instrumental methodology apart from the extraction temperature, nitroglycerin was not identified in the study by Gallidabino *et al.* [9], yet it was detected in the study by Weyermann *et al.* [13]. This could indicate that the selection of the target analytes may be of primary importance when selecting the extraction temperature. The fact, however, that both decreased and increased concentrations of different compounds were reported by Weyermann *et al.* [13] may pose a

challenge on the selection of the extraction temperature if quantification is the objective of the study.

Although SPME could be considered a well-established extraction method for OGSR compounds, for identification purposes and for the investigation of time since discharge, not all of the parameters of influence have been investigated equally thoroughly. Comparative studies of the SPME fibre types and extraction times indicate that both DVB/PDMS and PA fibres are suitable for the analysis of OGSR compounds and that an extraction time of around 35 min - 40 min may be used in combination with either fibre type. The majority of the parameters, however, predominantly the fibre type and extraction specifications, seem to be dependent on the selected target analytes.

A novel headspace sorptive extraction (HSSE) technique was tested for the sampling of volatile OGSR compounds from spent cartridges [9]. This method employs a magnetic stir bar as an extracting support. The extraction is based on the same principles as SPME, however, the stir bar is coated with a larger volume (up to 110 µL) of sorbent phase than an SPME fibre (maximum of 0.5 µL), making this a high capacity HSSE technique. The stir bars could be analysed using thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS). A desorption ramp in which the temperature was increased from 20°C to 250°C in two stages, taking a total time of 14.3 min, was used; as opposed to the isocratic desorption temperatures employed during SPME analyses reported in table 3.

In the study, this method was compared against SPME. The authors reported an increased reproducibility and effectiveness, in addition to a greater amount of compounds that could be simultaneously analysed using this novel HSSE method [9]. It must be noted, however, that a significant fraction of greater than 75% the compounds of interest are PAHs. As only nine other OGSR compounds have been included in this study (see table 1), the analysis of further OGSR compounds may be useful to establish the advantages of this method in the analysis of specific OGSR compounds.

2.1.2 Solvent extraction

Solvent extraction has been employed for the extraction of OGSR compounds from smokeless (propellant) powders [8, 10, 11] and spent cartridges [46], as well as OGSR compounds collected on a swab or (modified) stub [12, 53] and from vacuum collected samples [45]. Solvent extraction involves dissolving the sample by submerging the powder or object containing the OGSR sample in a solvent for a period of time. Dissolving the sample may be done in an aqueous solution [38, 46] or in organic solvents, such as methanol [8, 12, 14], methylene chloride [10, 11, 45], acetonitrile [10] or methyl ethyl ketone [54]. This process can be aided and thus accelerated, by stirring or (ultra)sonication [8, 14, 46]. Stirring, however, was considered to be ineffective by Zeichner and Eldar, who reported that sonication is imperative to achieving an efficient extraction [38]. This is generally followed by centrifugation, which allows for the collection of the supernatant and filtration [8, 14, 46]. Alternatively, the sample may be concentrated prior to centrifugation by blowing it to near dryness [38], or complete dryness [10-12]. In the latter case, the dry sample is reconstituted in a small amount of solvent. In this case, filtration of the sample may not be necessary [10-12]. Organic solvents used for reconstitution include single organic solvents such as methanol [12] or a mixture such as an acetonitrile and phosphate buffer [10]. In a study by Thomas *et al.* [11] a mixture of acetonitrile and water with 0.6 mM ammonium acetate and 0.02 mM ammonium chloride was used for the reconstitution of the sample.

Several aqueous and organic solvents have been tested for the extraction of OGSR compounds from double sided adhesive tape mounted on a stub by Zeichner and Eldar [38]. They also investigated the influence of sonication on the extraction efficiency at different temperatures: at and below room temperature for organic solvents and room temperature up to 80°C for aqueous solutions. It was found that the use of organic solvents resulted in considerable interference, brought on by adhesive components from the stub and skin components from the debris picked up

during the sampling of the skin [38]. This drawback has also been observed when using a swab soaked in an organic solvent for the collection of GSR from skin [2]. The interference was observed even at very low temperatures and with relatively short extraction times of several minutes. This problem was not observed when using aqueous solvents for the extraction. It must be noted that sodium azide (0.1% w/v) was added to the water part of the aqueous solutions to improve the stability of nitroglycerin. The major drawback of using water as a single solvent for the extraction is the relatively long extraction time and the low extraction efficiency. For example, an extraction method of 30 min sonication at 80°C resulted in a 10% recovery for nitroglycerin. The extraction time could be decreased, whilst improving the extraction efficiency, by using a mixture of water and 10% ethanol. Further optimisation of both parameters was observed when using a 20% ethanol in water mixture. According to this study, the best extraction method for recovery of OGSR from stubs employs a water/ethanol (80/20) mixture and sonication at 80°C for 15 min, followed by a further extraction with methylene chloride and concentration by evaporation [38].

Solvent extraction procedures are employed in conjunction with a wide array of analytical techniques including gas chromatography-mass spectrometry (GC-MS) [8], ultra-high performance liquid chromatography-tandem MS (UPLC-MS/MS) [11], high performance liquid chromatography – ultra violet detection (HPLC-UV) [14], liquid chromatography-quadrupole time-of-flight (LC-QTOF) [12], ion exchange chromatography [46], Raman microscopy [54], capillary electrophoresis (CE) [10] and micellar electrokinetic capillary chromatography (MEKC) [14]. The use of organic solvents, however, is both economically and environmentally disadvantageous [8]. Another disadvantage is the potential need to concentrate the sample and/or remove interfering compounds by using a clean-up method [2, 3], such as SPE, which may lead to reduced recoveries [2].

In summary, there is a wide variety of sampling and extraction techniques available for the collection of OGSR. Which collection method is most appropriate depends on the surface to be sampled, the target analytes selected and on the analytical method.

3. Analytical techniques

Analysis of OGSR has been performed since the early 1960s [55], using a wide array of analytical techniques. Several previous reviews have discussed these techniques which are summarised in table 4. Therefore, techniques that have already been considered elsewhere will only be briefly covered here. Where appropriate, for example due to less extensive coverage elsewhere, an overview of previous studies is given and new developments of these techniques, as well as new methods, will be discussed in more detail.

Table 4: Analytical techniques for OGSR detection

Type of technique	Technique	Acronym	Ref
Colour test	Colour/spot test	-	[2-4]
	Thin layer chromatography	TLC	[3, 56]
Spectroscopy	Fourier transform infrared	FTIR	[3, 56, 57]
Liquid chromatography			
detector combinations	Electron capture detection	HPLC-ECD	[2, 3, 56]
	Pendant mercury drop electrode	HPLC-PMDE	[2, 3]
	Mass spectrometry	HPLC-MS	[2, 3]
	Tandem mass spectrometry	LC-MS/MS	[2, 11, 56]
	Ultra violet detection	HPLC-UV	[2, 3]
	Fluorescence detection	-	[2, 3]
Gas chromatography			
detector combinations	Electron capture detection	GC-ECD	[3]
	Thermal energy analysis	GC-TEA	[2, 3, 47]

	Flame ionisation detector	GC-FID	[3, 47]
	Mass spectrometry	GC-MS	[2, 3, 8, 9, 13, 56]
Super critical fluid detector combinations	Ultra violet detection	SCF-UV	[3]
	Flame ionisation detector	SCF-FID	[3]
	Electron capture detection	SCF-ECD	[3]
Mass spectrometry	Time of flight - mass spectrometry	TOF-MS	[2, 12]
	Secondary ion mass spectrometry	SIMS	[2, 7]
	Ion mobility spectrometry	IMS	[2, 7, 50, 56, 58, 59]
	Focussed ion beam	-	[2]
Electrochemical detection	Capillary electrophoresis	CE	[2, 3, 10, 15]
	Micellar electrokinetic capillary electrophoresis	MECE	[2, 3, 14]
	Micellar electrokinetic capillary chromatography	MEKC	[2]

Colour tests may be attractive due to their inexpensive, simple and rapid nature, however, the major drawback of such methods is the fact the results are merely indicative. Consequently, these tests are used less frequently nowadays [2, 3].

FTIR has been used as a probe for the analysis of the distribution of OGSR in and around bullet entrance holes and to estimate firing distances [56]. It has also been used as a confirmatory technique after HPLC-UV analysis, to enable a positive identification of nitrocellulose [3, 60].

HPLC-UV can be used as a fast screening technique [3]. LC-MS and LC-MS/MS are useful tools for both the identification and quantification of OGSR compounds. Limits of detection of the latter technique have been reported in the low $nmolL^{-1}$ range for diphenylamine and related compounds, which corresponds to microgram levels. Sample concentration and purification may be necessary, which can be achieved with SPE [2].

Gas chromatography has been combined with several different detectors for OGSR analysis (table 4). The main advantage of GC analysis is the possibility for thermal desorption. In combination with SPME, the direct transfer of the preconcentrated compounds from the fibre into the GC inlet eliminates the need for additional extraction steps [47]. It should be noted that GC is only applicable to thermally stable volatiles and semi volatiles [2]. For example, nitrocellulose, the main component of modern smokeless powders, is incompatible with GC analysis due to the insufficient volatility of the compound [2, 3]. It may accelerate column deterioration if injected as a major component [2]. Thermal instability of compounds, such as nitrate esters, also poses analytical challenges. Nitrate esters are frequently encountered in GSR but their thermal instability and tendency to decompose on improperly prepared columns hampers GC analysis of these compounds. This is particularly true for pentaerythritol tetranitrate (PETN). In addition, GC has been reported to be unsuitable for the analysis of stabilisers such as n-nitrosodiphenylamine, because denitrosation to diphenylamine may occur under the high temperatures involved [2, 3]. However, for thermally stable (semi) volatile compounds GC is sensitive, highly selective, rapid and enables qualitative and quantitative analysis. GC in combination with TEA is reportedly most commonly employed for OGSR analysis [2]. GC-TEA increases the high sensitivity and selectivity of gas chromatography. Moreover, it has been reported not to require purification of vacuumed samples for the analysis of trace amounts of OGSR [3]. Detection limits in the low nanogram range have been achieved for dinitrotoluene-compounds. GC-MS has frequently been used in recent OGSR analyses and the majority of the detected organic compounds associated with OGSR has been detected from propellant powder and spent cases using this technique [8, 9, 13]. GC can also be coupled to IMS to enable the separation of complex

mixtures [59]. Detection limits of several nanograms per compound have been reported for GC-MS [2]. These limits are comparable to SPME-IMS [58].

A major advantage of TOF-SIMS is the ability to analyse both inorganic and organic compounds. It has been reported, however, to be unsuitable for more volatile compounds such as nitroglycerin, due to the high-vacuum conditions inside the instrument [2]. Different ionisation techniques for MS detection and their relation to OGSR analysis have been discussed by Taudte *et al.* [7].

CE can provide rapid, high-resolution separations of complex mixtures. Although electrically neutral compounds such as those found in OGSR cannot be separated by conventional CE [3], it has been used for the analysis of both inorganic and organic GSR analysis with limited success. Preconcentration did enable the detection of OGSR, however, it was concluded that separate runs for the inorganic and organic components may be a better option. Alternatively, MECE allows the separation of electrically neutral compounds [3] with limits of detection achieved by MECE for dinitrotoluenes and nitrodiphenylamines in the low picogram range for standard solutions [2]. MEKC in combination with UV detection is reported to be an interesting screening technique, due to the fact that it has a broader range of detected analytes, better suitability for diode array detection and lower operation costs than HPLC-UV [2].

3.1 Further development of current analytical techniques

Several of the techniques highlighted in table 4 have been further developed since the publications of the mentioned reviews [2, 3, 7, 56]. Although developments are not limited to a specific type of technique, significant progress has been made with a number of methods including IMS, HPLC-MS and CE. This indicates that a generic analytical approach for the analysis of OGSR has not yet been established.

3.1.1 Ion mobility spectrometry

Ion mobility spectrometry (IMS) is recognised as one of the most sensitive and robust techniques for explosive detection [61] and has been reported to be a good complementary technique to GC-TEA [2]. IMS has great advantages including enhanced sensitivity and selectivity, a very fast response time, low detection limits and field employability [61]. Despite this, relatively little investigation into the applicability of this method to the analysis of GSR has been undertaken, although some studies in the early 2000s have reported the use of IMS for the detection of OGSR [38, 45, 61, 62]

Previously, Colón *et al.* [61] used IMS for the detection of smokeless powders using a collection filter in combination with thermal desorption for sample introduction. Nitroglycerin, nitrocellulose and nitrate were detected. Neves *et al.* [62] used Ion Trap Mobility Spectrometry for the detection of smokeless powders based on ethyl centralite. The performance of IMS for the detection of OGSR compounds, collected after firing tests, was studied by Zeichner *et al.*, who demonstrated the feasibility of OGSR analysis with IMS from vacuum collected samples [45] and from double-side adhesive coated stubs [38].

A significant improvement of the applicability of IMS to the analysis of volatile OGSR was the development of an interface enabling the combination of IMS with SPME, which was reported in 2005 [58]. Detection limits achieved by standard IMS were around 20 ng for most tested compounds, compared to below 1 ng for all tested compounds when using SPME-IMS [58]. The development of a new, energy-conserving interface increased the feasibility of field analysis with SPME-IMS [63]. Another attempt to increase the suitability of SPME-IMS for field analysis involved a different approach to selecting compounds of interest. Instead of focussing on the parent molecules of explosives, which may be incompatible with SPME due to lack in volatility, the target analytes selected by Lai *et al.* [64] are so called odour signature compounds; volatile odour chemicals associated with the explosive. Limits of detection are reported in the low nanogram range [64]. Further development of this approach by Joshi *et al.* [65] involved the analysis of odour signature compounds which are characteristic for smokeless powders. This gives rise to the potential of a

simultaneous screening and confirmatory technique. Only four OGSR compounds have been included in this study, however and the results are thus still only presumptive identifications of OGSR [65].

Joshi *et al.* [50] used SPME-IMS for the identification of volatile and semi volatile additives of smokeless powders. It is reported that all peaks are sufficiently resolved, however, only eight target analytes have been detected using IMS. Separation of compounds may be an issue when more target compounds are present. A possible solution to this issue could be the use of a differential mobility analysis (DMA), which is a specific configuration of an IMS which facilitates the improvement in resolving powder and sensitivity, although it was not tested specifically for OGSR compounds [66]. Alternatively, IMS has been combined with GC to provide the separation of complex mixtures [59]. Although this inhibits field analysis, a reduction in false positives was demonstrated in a study by Cook *et al.* [59].

These studies seem to confirm the potential for the use of IMS in the analysis of OGSR. The advantages specific to IMS, especially the field-portability and near instantaneous analysis speeds, make IMS particularly suitable as a rapid, on site screening technique. Two anticipated difficulties of this technique are: the potentially insufficient separation power for complex mixtures, or when a greater amount of OGSR compounds is to be included in the analysis; and the lesser suitability as a confirmatory technique [59]. In a recent study by Arndt *et al.* [67], however, IMS was used for the analysis of OGSR, which was collected from the shooter's hands using a swab. The identification of GSR was based predominantly on the presence of DPA, which was absent in the blank samples [67]. This further confirms the strength of IMS as a rapid and viable screening tool.

3.1.2 Ultra performance liquid chromatography tandem mass spectrometry

A further development of LC-MS is the use of ultra-high performance liquid chromatography (UPLC). In a study by Thomas *et al.* [11] UPLC was employed for the separation of 21 OGSR compounds, providing faster separation and increased resolution. Moreover, an optimised tandem MS method enabled the detection of both positive and negative ions, allowing the analysis of all compounds of interest in a single run. This was achieved by employing two ionisation sources: electrospray ionisation (ESI), in both positive and negative mode and atmospheric pressure chemical ionisation (APCI) in negative mode and switching between them at high speeds. This resulted in the detection of 18 of the target analytes in a total run time of under 8 minutes [11].

3.1.3 Desorption Electrospray Ionisation

The major advantages associated with desorption electrospray ionisation (DESI) are its capability of direct analysis of solid surfaces without the need for sample preparation and the compatibility with portable mass spectrometers [68]. These advantages, in conjunction with the real time analysis capability of DESI-MS, its simplicity and the high throughput, give rise to a potential screening application of this technique. Furthermore, the potential of DESI-MS to supply structural information in real time [68] could enable the combined function as a screening and confirmatory technique, possibly even in a single run.

Zhao *et al.* [68] used DESI-MS/MS successfully for the detection of subnanogram levels of OGSR compounds, based on the presence of methyl centralite (MC) and ethyl centralite (EC), from several solid surfaces including a human hand. They reported no interference from the tested surfaces and were able to detect OGSR for up to 12 hours and hands could be washed at least six times. The only disadvantage mentioned is the fact that the DESI source contains a high voltage component, which is potentially harmful to the analyst. Appropriate shields and interlocks were required to prevent accidental contact, which may make this piece of equipment more suitable for use in contained environments. It should be noted that the detection in this study is based on merely two OGSR components. The evidential value of this technique would significantly increase with the inclusion of several additional OGSR compounds. The authors stated, however, that the

capability for this is present, based on previous studies that used DESI-MS for the detection of for example diphenylamine (DPA) and its nitration products from propellant powders [68, 69].

This potential is somewhat confirmed by the detection of MC, EC and DPA from smokeless powder by nanoDESI-MS/MS [70]. These compounds were also detected in OGSR from cotton cloths, however, interference which was most likely due to the presence of detergent was observed in the analysis of machine-washed and dried cloths.

Morelato *et al.* [71] reported the detection of MC, EC and DPA by DESI-MS on adhesive stubs typically used for the analysis of IGSR compounds by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX). They found that the DESI-MS analysis did not significantly interfere with this SEM-EDX detection, enabling the analysis of OGSR and IGSR from a single sample, though by different techniques. As a disadvantage they reported the relatively high detection limits, which are due to the characteristics of the stub.

A possible solution to this problem is the use of a collection and preconcentration step [72] developed by Venter *et al.* [73]. This surface sampling technique decouples desorption from analysis, to enable the collection of the spray onto a suitable secondary surface. Subsequent analysis can be performed by direct ambient ionisation mass spectrometry (as is the case with standard DESI-MS), or by other techniques, such as GC-MS and UV spectroscopy.

3.1.3 Raman spectroscopy

The application of Raman spectroscopy to the analysis of OGSR compounds was first reported in 2012 [54, 74]. It was successfully used for the detection of MC, EC, dinitrotoluene, DPA and its nitration products [54, 74]. The authors reported that the OGSR spectrum showed high similarity with the spectrum of the unfired ammunition, which enabled the OGSR to be traced back to the ammunition used. Other substances, which might be confused with GSR materials such as sand, dried blood, or black ballpoint ink were easily distinguishable from GSR, confirming its screening capability [54].

Raman spectroscopy was also used in conjunction with a statistical analysis, which demonstrated that the obtained spectra could provide highly accurate identifications of ammunition calibre-firearm pair, when subjected to the statistical classification analysis. This study was performed from the point of view that the specific firearm parameters are responsible for the combustion process and that the chemical composition of specific ammunition is dependent upon the calibre and that as such this calibre-firearm pair would determine the subsequent GSR product. The authors reported the potential for a rapid, portable, solventless and selective alternative for GSR identification, while providing a statistical and chemical link between the suspect and the crime scene [74]. In order to further improve the statistical discrimination of GSR, complementary spectroscopic data from Raman and Fourier Transform Infrared FTIR spectroscopy were combined into a single dataset, in a later study by Bueno and Lednev [75].

Abrego *et al.* [53] reported a micro-Raman spectroscopy method for the analysis of OGSR. The total analysis time, including the parallel analysis of IGSR with another technique, was 2 hours due to the fact that the observation of the GSR particles via optical microscopy for the subsequent analysis by Raman spectroscopy was performed manually. A decrease in the analysis time is expected if this step can be automated using image recognition software.

3.2 Full chemical profiling

The ability to combine organic and inorganic GSR information would significantly increase the probative value of GSR evidence [5]. Consequently, several attempts to realise this have been undertaken. The analytical instrumentation generally used for the analysis of either OGSR or IGSR presents two major challenges: the inability of the techniques to analyse both organic and inorganic compounds, which gives rise to the need for the analysis of a single sample by multiple techniques and the destructive nature of most analytical techniques, which hampers sequential analysis of the same sample.

One proposed solution is the use of modified stubs in which half of the stub's surface is used for the analysis of IGSR and the other half for OGSR analysis. This approach was used by Abrego *et al.* to analyse both halves simultaneously with Raman microscopy (OGSR) and scanning laser ablation-inductively coupled-mass spectrometry (IGSR) [53] and by Benito *et al.* for the simultaneous analysis with LC-QTOF (OGSR) and SEM-EDX (IGSR) [12].

Another approach is the analysis of OGSR with a non-destructive technique, which allows subsequent IGSR analysis. OGSR analysis with DESI-MS followed by SEM-EDX for IGSR analysis, as suggested by Morelato *et al.* [71], is an example of this.

The key objective would be the development of an analytical technique that can analyse both organic and inorganic compounds. So far, three analytical techniques have been described for this purpose: electrochemical detection [5], Raman spectroscopy [74] and FTIR spectroscopy [57].

The electrochemical detection of IGSR and OGSR proposed by Vuki *et al.* [5] includes four metals (IGSR) and three OGSR compounds. Their method employs electrochemical devices that are described as sensitive, compact, low-power and easy to use and thus particularly attractive for field analysis. The results were rapidly generated in a single scan for both organic and inorganic compounds, which was reported to be an information-rich, inorganic/organic electrochemical fingerprint [5]. The inclusion of a limited number of organic compounds, however, is likely to be insufficient to provide an accurate, reliable GSR fingerprint. The authors reported to aim for the inclusion of a few more compounds but potential coelution is expected to pose challenges [5]. This suggests that this method may not be suitable when more compounds are included to decrease the chances of false positives and strengthen the reliability of the results. Furthermore, it should be noted that the reported results have been obtained using standard mixtures rather than actual GSR. Consequently, the complexity of a real GSR mixture may pose significant challenges for the method. These issues indicate that such an 'on-the-spot' field method may have more potential as an initial screening technique.

Simultaneous detection of IGSR and OGSR using spectroscopic techniques has also been reported [57, 74], however, a limited amount of GSR compounds have been included in these studies. Raman spectroscopy was used for the analysis of an unknown amount of OGSR compounds, predominantly nitrate esters and nitrotoluenes. Although the reported results were promising as they enabled differentiation between GSR from two ammunition-firearm combinations, it was unknown which specific characteristics resulted in the differentiation [74]. FTIR spectroscopy [57] was also based only on nitrate ester compounds and 2,4-DNT specifically. Consequently, further development of these spectroscopic methods is required, focussing on the inclusion of a wider selection of (O)GSR compounds and identification of the compounds on which differentiation between samples can be evaluated.

3.3 Overview of developments

The many different types of techniques that have been investigated with respect to the applicability to OGSR analysis demonstrate that no generic analytical approach to the analysis of OGSR has been established to date. Table 5 contains a brief overview of the advantages and disadvantages of the recent analytical developments discussed. In addition, greater amount of progress has been made with the MS based techniques included in this table, whilst applications of EC, Raman and FTIR spectroscopy still require further development before they can compete successfully with the other methods.

Table 5: Advantages and disadvantages of recent analytical developments in OGSR analysis

Technique	Advantages	Disadvantages	Ref
SPME-GC-MS	Simultaneous extraction and preconcentration Simple method No solvents required Applicable to solid, liquid and gaseous samples Over 70 OGSR compounds already detected Confirmatory technique	Laboratory based technique Relatively slow (around 30 min) Unsuitable for non-volatiles	[8, 9, 13, 50, 51]
UPLC-MS/MS	Relatively fast (8 min) Better resolution than HPLC-MS Positive and negative ions in single run Around 20 OGSR compounds already detected Confirmatory technique	Laboratory based technique Not applicable to airborne samples Laborious sample preparation Solvents needed	[11]
IMS	Rapid (seconds) Real time analysis Portable/field deployable Structural information Compatible with SPME & swipe method Low detection limits Simple method	May be unsuitable for complex mixtures More false positives than GC-MS	[50, 58, 59, 61-66]
DESI-MS	Rapid (seconds) Real time analysis Portable/field deployable Structural information No separate sample prep or collection method required Subsequent SEM-EDX on same sample possible Simple method	May be unsuitable for complex mixtures Only four OGSR compounds tested Not applicable to airborne samples	[68, 70-73]
Raman/ FTIR	Non-destructive OGSR and IGSR	Laboratory based technique Further development needed	[53, 54, 57]
EC	IGSR and OGSR in a single run Potentially field deployable Rapid Sensitive Simple method	Not yet tested on GSR Only four OGSR compounds included Potential peak overlap when adding compounds	[5]

4. Summary

The analysis of OGSR is a field of ongoing, need-driven development and increasing applications. This review has highlighted several aspects with regard to the analytical techniques and methodologies used in the detection of OGSR compounds.

Extracting as much information as possible from GSR samples would increase the value of GSR investigations, because it increases the probability of accurate interpretation. Consequently, the inclusion of both organic and inorganic GSR is favourable, which poses two main challenges on the analysis: the inability of techniques to analyse both organic and inorganic compounds, which gives rise to the need of the analysis of a single sample by multiple techniques; and the destructive nature of most analytical techniques, which hampers sequential analysis of the same sample. Possible solutions may be provided by sampling/extraction techniques which enable the separate, yet simultaneous analysis of the OGSR and IGSR halves of the sample, such as a modified tape lift method. OGSR analysis can be performed using laboratory based techniques such as GC-MS and UPLC-MS/MS, which are capable of separating complex mixtures; or field deployable techniques such as IMS and DESI-MS, which enable rapid, on site analysis. Another possibility is the use of a non-destructive technique for the analysis of the organic compounds, such as DESI, to allow for subsequent analysis of the same sample for inorganics. Improvements in detection of OGSR and IGSR compounds within a single analysis have also been made, utilising electrochemical detection, Raman microscopy and FTIR spectroscopy. However, further development and inclusion of a more substantial number of (O)GSR compounds is required.

There is a range of analytical techniques available for OGSR analysis, together with corresponding sample collection and extraction procedures. The difficulty in selecting an appropriate analysis method lies in the many variables which affect the performance of each technique. Consequently, the choice for an optimal methodology for any OGSR sample calls for a ‘case-by-case’ approach, in which the purpose of the investigation should be the predominant factor.

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