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Recent trends in organic gunshot residue analysis

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A B S T R A C T

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. We highlight recent developments in both extraction and analytical methods employed for their detection. The main advantages and disadvantages of the sampling and analysis methods are critically discussed.

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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 the propellant, as well as the cartridge case, the projectile jacket and its core, and the gun barrel [1,2].

Present analysis methods of GSR in forensic investigations mainly focus on inorganic GSR (IGSR) analysis using scanning electron

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Abbreviations

Techniques and parameters

APCI	Atmospheric pressure chemical ionization
ATR	Attenuated total reflectance
CE	Capillary electrophoresis
DESI	Desorption electrospray ionization
DMA	Differential mobility analysis
ECD	Electron-capture detection
EDX	Energy-dispersive X-ray spectroscopy
ESI	Electrospray ionization
FID	Flame ionization 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	Supercritical fluid
SEM	Scanning electron microscopy
SIMS	Secondary ion mass spectrometry
SPE	Solid-phase extraction
SPME	Solid phase microextraction
TD	Thermal desorption
TEA	Thermal energy analysis
TLC	Thin-layer chromatography
TOF	Time of flight
UPLC	Ultra-performance liquid chromatography
UV	Ultraviolet

Compounds and chemicals

AKI	Akardite I
AKII	Akardite II
AKIII	Akardite III
BP	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	Polycyclic aromatic hydrocarbon
PDMS	Polydimethylsiloxane
PETN	Pentaerythritol tetranitrate
RDX	Cyclonite
TNT	2,4,6-Trinitrotoluene

microscopy (SEM) methodologies [1,4]. However, combining this information with organic GSR (OGSR) information would significantly increase the probative value of GSR evidence [5], as it enables more accurate interpretation of the analytical results obtained [2].

This review discusses organic compounds that could be associated with smokeless powders and GSR. We highlight recent developments in both extraction and analytical methods employed for their detection. Fig. 1 gives a brief overview of key milestones in OGSR analysis.

1.1. OGSR compounds

Dalby et al. [2] produced a comprehensive list of 48 organic compounds that may contribute to GSR 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 GSR. 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.

Table 1 compares the compounds listed in the mentioned reviews by Dalby et al. [2] and Taudte et al. [7] against several experimental studies on OGSR compounds. The majority of these studies have been reported since 2010 [2,7,9,10,12–14]. A few studies, including one review [3], prior to 2010 have been included for the purpose of comparison [8,15,16]. This has resulted in a list containing 136 organic compounds that could be associated with smokeless powders and GSR.

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 [8,10].

PAHs are widespread, persistent and ubiquitous environmental pollutants [17–19], which can exist in both vapor 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 OGSR is very limited. However, it must be noted that the specific studies including these compounds [8,10] did not aim for the identification of GSR 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. [10] 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 normalization of the determined aging curve.

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