



Characterization of organic gunshot residues in lead-free ammunition using a new sample collection device for liquid chromatography–quadrupole time-of-flight mass spectrometry

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ABSTRACT

The identification of characteristic organic gunshot residues (OGSR) provides conclusive evidence in the elucidation of elemental profiles when lead-free ammunition is fired. OGSR also prevents false negatives. Toward this aim, a quick and efficient method based on liquid chromatography–quadrupole time-of-flight mass spectrometry (LC–QTOF) was developed to detect and identify 18 gunpowder additives in gunshot residues (GSR). The unequivocal identification of target analytes was assured by using MS/MS mode. Swabs were compared with home-modified tape lift supports covered with a PTFE layer to determine the better sampling technique. The modified tape lift provided better extraction recoveries and enabled the analysis of inorganic and organic GSR simultaneously. The developed method was applied to the analysis of GSR from four different lead-free ammunitions. Diphenylamine and its nitrated degradation products and centralites were identified in all samples, providing strong evidence of GSR.

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1. Introduction

Gunshot residues (GSR) are unburned and partially burned particles that can arise from the primer, propellant, primer components, lubricants and metals contained in the projectile and in the gun barrel after a gun is fired [1]. The identification of GSR provides very important evidence in forensic investigations. Notably, GSR has been used to pinpoint suspects, differentiate homicide and suicide, and even to estimate the firing distance and to determine a bullet hole [2].

The chemical analysis of GSR can be focused on inorganic or organic components. To date, inorganic GSR has been widely investigated. Inorganic GSR is composed of nitrates, nitrites and metallic particles mainly generated from the primer and propellant. According to standard criteria from the ENFSI (European Network of Forensic Science Institute) and the ASTM (American Society for Testing and Materials), elemental analysis is the most accurate method for identifying GSR. Moreover, particles with a combination of Pb, Sb and Ba are considered to be “characteristic of

GSR” [3,4]. Scanning electron microscopy equipped with an X-ray detector (SEM–EDX) has been the method of choice in analysing the elemental profile of GSR particles [5]. Recently, an alternative method based on laser ablation coupled to inductively coupled plasma–mass spectrometry (LA–ICPMS) has been proposed [6].

Organic components are predominantly originated from the propellant and the primer mixture and their identification may strengthen the probative value of a sample [1,7,8]. The main propellants used in firearms are smokeless powders that almost exclusively contain nitrocellulose (NC) as the main explosive component in single-base powders, NC and nitroglycerine (NG) in double-base powders and NC, NG and nitroguanidine (NQ) in triple-base powders [1]. After the firearm is discharged, NC and NG are rapidly decomposed [9,10]. The decomposition products are very common in many explosives which limits their use in identifying explosives [11]. In addition to these explosive compounds, smokeless powders contain additives such as stabilizers, plasticizers, flash inhibitors, coolants, deterrents, surface lubricants, dyes and other components that may contribute to the composition of organic gunshot residues (OGSR) (Table 1).

To date, most of the studies published on the identification of organic components in smokeless powders are based on the analysis of unburned propellants powders. Notably, only a few

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Table 1
Common organic components of smokeless gunpowder.

Explosives	Nitrocellulose (NC), nitroglycerine (NG), nitroguanidine (NQ), cyclonite (RDX), octogen (HMX), 2,4-dinitroanisole (DNAN)
Sensitizers	Trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN)
Stabilizers	Diphenylamine (DPA), methyl centralite (MC), ethyl centralite (EC)
Flash inhibitors	2,4-dinitrotoluene (2,4-DNT), nitroguanidine (NQ)
Plasticizers	Diethyl phthalate (DEP), dimethyl phthalate (DMP)
Degradation products	2-Nitrodiphenylamine (2-NDPA), 4-nitrodiphenylamine (4-NDPA), 2,4-dinitrodiphenylamine (2,4-DNDPA), N-nitrosodiphenylamine (N-NDPA), 2-amine-4,6-dinitrotoluene (2-ADNT), 4-amine-2,6-dinitrotoluene (4-ADNT)

studies propose operational methods sensitive enough to identify OGSR on shooter's hands. Gas chromatography coupled with flame ionization detector (FID), thermal energy analysis (TEA), electron capture detector (ECD) and mass spectrometry (MS) have been applied to OGSR analysis [1,2]. Nevertheless, thermal decomposition of NG [12] and nitrate esters [2] and denitrosation of nitrosodiphenylamines caused by high temperatures have been observed [13]. In addition, NC is not sufficiently volatile. As a result, it is incompatible with the standard conditions employed in GC systems [12].

Wu et al. reported the use of liquid chromatography tandem mass spectrometry (LC-MS/MS) in the analysis of diphenylamine and its nitrated derivatives in gunpowders [14] and methylcentralite in GSR, recovered from shooter's hand by using cotton wool swabs soaked in methanol [15]. Some years later, Laza et al. [10] developed an LC-MS/MS method for the analysis of the propellant powder stabilizers, DPA, N-nitrosodiphenylamine (N-NDPA), 4-nitrodiphenylamine (4-NDPA), 2-nitrodiphenylamine (2-NDPA) and ethylcentralite (EC), in residues found on a shooter's hands. However, a solid-phase extraction (SPE) stage was required to concentrate and purify the collected OGSR, increasing the risk of sample contamination during handling. Recently, Thomas et al. [16] developed a method based on UPLC-MS/MS to analyze a broad range of smokeless powder additives. Nevertheless, this method was only applied to the characterization of different types of smokeless powders and its suitability for studies involving GSR analysis was not demonstrated.

As an alternative, Raman spectroscopy combined with advanced statistics has been used to differentiate the ammunition caliber [17] and to trace the GSR obtained from target cloths to the ammunition used [7]. Both methods were based on "case-by-case" assessment procedures. However, Raman spectroscopy requires the localization of individual GSR particles and it is not sensitive enough for some compounds (e.g. plasticizers) [9].

"Lead-free" or "non-toxic" ammunition was released to the market amid concerns over health problems related to airborne pollution and exposure to high levels of heavy metals. However, this ammunition prevents the unambiguous identification of GSR based on the ENFSI's criteria and a case-by-case approach is recommended [18]. In these cases, the identification of characteristic organic compounds from gunpowder after a gun is fired provides conclusive information that enables discrimination between GSR and environmental particles. Therefore, analyzing both inorganic and organic residues in the same sample becomes essential when "lead-free ammunition" has been fired. Tape lifting is the most common technique used for sampling inorganic residues, while swabbing has mainly been used to collect organic compounds.

The goal of the present study was to develop a rapid and sensitive approach to analyze a broad range of organic GSR compounds collected from shooter's hands, which would provide additional and conclusive information in the analysis of inorganic particles. To unequivocally confirm the presence of the most characteristic smokeless powder additives, a liquid chromatography/quadrupole time-of-flight mass spectrometer (LC-QTOF) was used in the MS/MS mode. In this sense, QTOF is unique in its ability

to give accurate mass measurements of the fragment ions that are ejected from the collision chamber, giving high assurance of correctly identified target analytes [19]. Moreover, working in MS/MS mode enhances sensitivity and decreases the background noise, enabling the identification of low amounts of OGSR.

The present findings have been applied to the identification of 18 compounds commonly found within smokeless powders. These compounds include explosives such as nitroguanidine (NQ), octogen (HMX), cyclonite (RDX), 2,4-dinitroanisole (DNAN), trinitrotoluene (TNT) and pentaerythritol tetranitrate (PETN); stabilizers such as methylcentralite (MC), ethylcentralite (EC) and diphenylamine (DPA); plasticizers such as dimethyl phthalate (DMP) and diethyl phthalate (DEP); flash inhibitors such as 2,4-dinitrotoluene (2,4-DNT); and some metabolites or degradation products such as N-nitrosodiphenylamine (N-NDPA), 4-nitrodiphenylamine (4-NDPA), 2,4-dinitrodiphenylamine (2,4-DNDPA), 2-nitrodiphenylamine (2-NDPA), 2-amine-4,6-dinitrotoluene (4-ADNT) and 4-amine-2,6-dinitrotoluene (2-ADNT).

To select the most suitable OGSR sampling method from shooters' hands, the collection efficiency of swabbing and the home-modified tape lifting method were compared. Finally, GSRs from four different lead-free primer ammunitions were analyzed to verify the applicability of the developed procedure.

2. Material and methods

2.1. Chemical and reagents

Ammonium acetate (98%) and LC-MS grade methanol used in the mobile phase were supplied by Acros Organics (Morris Plains, NJ, USA) and Scharlau (Barcelona, Spain) respectively. To optimize the pre-treatment procedure, 2-propanol multi-solvent HPLC grade (Barcelona, Scharlau) and dry acetone (max. 0.01% H₂O) from Panreac (Barcelona, Spain) were used. All solutions were prepared with ultra-high purity water (UHP) obtained from tap water pre-treated by Elix reverse osmosis cartridges prior to filtration by a Milli-Q system from Millipore (Bedford, MA, USA).

Standards of DNAN, 2-ADNT, 4-ADNT, 2,4-DNDPA, 2-NDPA, N-NDPA and 4-NDPA were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). HMX, RDX and PETN were supplied by AccuStandard[®] Inc. (New Haven, USA). DPA, DMP, EC, 2,4-DNT and NQ were provided by Sigma-Aldrich (Steinheim, Germany). DEP and MC were purchased from Alfa Aesar (Karlsruhe, Germany) and MP Biomedicals (Illkirch, France) respectively. TNT was obtained from the Institute of Industrial Organic Chemistry from Warsaw (Poland).

Stock solutions containing 1 mg mL⁻¹ of individual analyte standards were prepared in methanol and they were preserved at -42 °C in a freezer. Further dilutions down to 1 mg L⁻¹ were also carried out with methanol and stored at 4 °C. Working standard solutions were prepared by diluting the appropriate volume of the 1 mg L⁻¹ reference solution up to 10 mL with water. To optimize the method, a standard solution, containing 1500 ng mL⁻¹ of DPA, DMP and 2,4-DNT, 400 ng mL⁻¹ of NQ, TNT, PETN, N-NDPA and 2-NDPA, 5 ng mL⁻¹ of EC and MC and 30 ng mL⁻¹ of the remaining analytes was prepared.

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