



## Characterisation of gunshot residue from three ammunition types using suppressed anion exchange chromatography

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### ABSTRACT

Gunshot residue (GSR) is commonly analysed in forensic casework using either scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) or gas chromatography-mass spectrometry (GC-MS). Relatively little work has been reported on the post-discharge GSR content of non-metallic inorganic or low molecular weight organic anions to distinguish between different ammunition types. The development of an analytical method using suppressed micro-bore anion exchange chromatography (IC) is presented for the analysis of GSR. A hydroxide gradient was optimised for the separation of 19 forensically relevant organic and inorganic anions in <23 min and sensitivities of the order of 0.12–3.52 ng of anion detected for all species were achieved. Along with an optimised extraction procedure, this method was applied to the analysis of post-ignition residues from three selected ammunition types. By profiling and comparing the anionic content in each ammunition residue, the possibility to distinguish between each type using their anionic profiles and absolute weight is presented. The potential for interference is also discussed with respect to sample types which are typically problematic in the analysis of GSR using SEM-EDX and GC-MS. To the best of our knowledge this represents the first study on the analysis of inorganic anions in GSR using suppressed ion chromatography.

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### 1. Introduction

Gunshot residue (GSR) is the material emitted by ammunition during discharge. This includes particles from the primer, propellant, as well as metals from the cartridge case and barrel of the gun, which can be deposited on nearby surfaces as particles or as condensing vapours. Analytical methods are well established for metallic GSR identification, such as inductively coupled plasma mass spectrometry (ICP-MS) [1] and neutron activation analysis (NAA) [2], with the most common being scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) [3,4]. This technique enables identification of GSR particle morphology as well as elemental composition [5]. With the potential to identify and characterise even 1 µm diameter particles, this is a very useful tool used in practical forensic casework [3]. However that said, analysis times are often lengthy (several days), and SEM-EDX is generally only used to examine the metallic particles found in GSR, commonly lead, antimony and barium. It is not possible to speciate anionic counter ions with this technique. False positives have also been observed with signature

particles appearing in fireworks [6] and residues on used vehicle brake linings [7]. More recently, the emergence of primers free from heavy metals [8], has meant that the possibility for false negatives has also increased. With firearms reported to have been involved in over 11,000 recorded crimes in 2010/11 in England and Wales [9], this indicates a potential requirement for the determination of components other than traditional metallic residues to further strengthen the evidential value of GSR analyses. Organic compounds present in GSR have also been used for this purpose. These compounds include nitroglycerine and isomers of dinitrotoluene which originate mostly from the propellant. Gas chromatography (GC) [11,12], high performance liquid chromatography (HPLC) [13] and capillary electrophoresis (CE) [14] have all been applied to the analysis of organic components of GSR and GC coupled with thermal energy analysis (TEA) or mass spectrometry (MS) are the most prominent. However, this technique requires compounds to be volatile and thermally stable and therefore can be unsuitable for some compounds, such as nitrocellulose [10]. Furthermore, loss of organic compounds over several hours has been shown, making this type of analysis time-dependent. This obviously could be useful in determining the interval after firing, but where this time-period is too great; residues may be lost through molecular volatility, degradation or physical transfer.

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Rather surprisingly, a lack of published work exists on the determination of low molecular weight non-metallic anionic species in GSR using ion chromatography (IC). Furthermore, little is known of the forensic significance of these species in GSR. IC has been used more recently for the identification of components in improvised explosive devices (IEDs) and has shown it can sensitively and robustly determine inorganic charged species [15]. Johns et al. separated 18 anions commonly found in inorganic explosives using suppressed IC with a hydroxide gradient, showing it was possible to distinguish between explosive types [16]. With primer mixes typically made from metal sulphides, nitrates, thiocyanates and chlorates, GSR shows some similarity in its potential energetic material ingredients to those used in IEDs, though is likely to be somewhat more complex given the number of ingredients used commercially. The ability to speciate gives IC an obvious advantage over current methods. Kolla also investigated the use of IC for explosives, using a potassium hydrogen phthalate eluent, focussing on chloride, nitrate and sulphate [17]. It was not practically possible to analyse real samples containing complex mixtures of anions in soil matrices, as the level of interference was too significant. As many similar ions were present in the environment, internal ratios between a typically non-explosives related anion and an energetic anion were calculated to attempt to eliminate environmental influences and to determine whether the explosive residue could be detected. Previous work by Wheals and Ellison demonstrated that it was possible to use anion exchange chromatography to determine the quantity of nitrite and nitrate anions generated through degradation of nitrocelluloses and nitroglycerine (commonly present in propellants). This study also showed that their relative concentration ratios could be significant in determining their source [18]. With regard to GSR in particular, ion ratio profiles could also be important when studying primer composition especially between anions other than nitrite and nitrate [10]. As primers and propellants differ among manufacturers, anion content is likely to differ, and could provide a means to distinguish between ammunition types.

To show the technology in practice, we recently reported the use of capillary-bore IC to detect energetic material residues in latent human fingerprints. Ion content in GSR was compared to those found in GSR-contaminated fingerprints deposited on glass substrates after discharge of a firearm. It was possible to detect pg-fg levels of anionic GSR species in fingerprints indicating that the technique could potentially be used for identification of these species in trace evidence. Furthermore, nitrate, benzoate and perchlorate could be detected at ng- $\mu$ g levels in fingerprints where the donor had been in direct contact with a black powder substitute used in muzzle-loading rifles. However, in order to derive any forensic conclusions, more work is required to determine the range of ion masses present in a larger sample set of ammunition to reliably propose relative ion ratios and associated limits of variation. This approach therefore does show promise for use within forensic science and is not limited to determinations made at relatively high concentrations.

CE also has the ability to speciate anions, and has also been used in the analysis of IED materials. Recent work by Hutchinson et al. has shown that it is possible to separate 15 anions in 7 min and 11 cations commonly found in explosives in <7 min using a portable CE system with capacitively coupled contactless conductivity detection (C<sup>4</sup>D) [19]. Whilst the sensitivity of the C<sup>4</sup>D was shown to be more sensitive than the more traditional indirect photometric detection, limits of detection (LODs) are still approximately an order of magnitude higher than when using IC. Detection at this higher level may be sufficient when marker ions are in mg/L range, but when a technique is needed to differentiate between residues containing trace quantities, suppressed micro-bore IC offers the sensitivity required. CE has also

been used by Morales et al. to analyse GSR by micellar electrokinetic chromatography (MEKC). Sodium dodecyl sulfate (SDS) was used to create anionic micelles, and diaminocyclohexane tetraacetic acid (CDTA) as a complexing agent to simultaneously separate 10 metal ions and 11 organic components of GSR using a diode array UV-vis detector. However, no inorganic anions were included in this study, and the LODs were not sufficient to detect important cations, such as barium and antimony, as well as low level organic residues, when run simultaneously [20]. CE is complementary to IC in many ways, and it is advantageous to use both techniques in a forensic context [16].

The aim of this work was to develop a sensitive suppressed micro-bore anion exchange chromatography method to characterise and quantify anions in GSR from three different ammunition types. Secondly, their forensic significance was determined by examining their relative ion mass ratios and any potential sources of interference. To the best of our knowledge, this represents the first comprehensive investigation of low-molecular weight anionic components in GSR by micro-bore IC.

## 2. Materials and methods

### 2.1. Reagents

All reagents were of analytical or reagent grade. Chloride, nitrite, nitrate, (BDH Chemicals Ltd., Poole, UK), fluoride (MP Biomedicals, Solon, OH, USA), chlorite (Acros Organics, Geel, Belgium), chlorate, perchlorate, bromate, cyanate and thiosulphate (Sigma-Aldrich, Gillingham, Dorset, UK) were prepared from their sodium salts; sulphate was prepared from its copper salt (BDH). Phosphate standards were prepared from its potassium salts (BDH); carbonate and threonate were prepared from their calcium salts (Sigma); acetate (BDH), and thiocyanate were prepared from their ammonium salts, with formate being prepared from an ammonium solution (Sigma). Lactate, oxalate (BDH), phthalate, quinate, ascorbate and benzoate (Sigma) were prepared from their acids. All stock solutions were prepared to a concentration of 1000 mg/L and working standards were prepared daily from these using deionised water. Eluents were prepared using a 50% NaOH solution in H<sub>2</sub>O (Sigma) for anion exchange chromatography. Where necessary, all eluents, stocks, standards and samples were prepared using ultrapure water (18.2 M $\Omega$  cm) delivered from a Millipore Milli-Q water ultra-purification system (Millipore, Bedford, MA, USA) and were filtered (0.45  $\mu$ m mesh) and degassed before use where appropriate. Chlorate, perchlorate, nitrite, cyanate, phosphate and organic acids stock standards were kept in the dark at 4 °C and were re-prepared fortnightly.

### 2.2. Instrumentation

Suppressed anion exchange chromatography was performed on a Dionex DX500 system (Dionex, Sunnyvale, CA, USA), comprising of a GP40 pump and an ED40 conductivity detector fitted with a Dionex ASRS 300 (2 mm ID) electrolytic suppressor (current = 50 mA). For anion separations involving eluents containing organic solvents, a Dionex AMMS III (2 mm ID) was used with a 0.5 mL/min regenerant flow of 50 mM H<sub>2</sub>SO<sub>4</sub> delivered by a Gynkotek 300 high precision pump (Gynkotek, Softron, Germering, Germany). Instrument control and data acquisition were performed using Chromeleon 6.6. In order to achieve acceptable anion sensitivity, the injection volume was 40  $\mu$ L. Two quaternary ammonium-based anion exchangers were investigated, a Dionex IonPac AS11 (2 mm  $\times$  250 mm) and an IonPac AS20 (2 mm  $\times$  250 mm). The optimised method using the IonPac AS20 was set at a flow rate of 0.35 mL/min. In order to separate all species, a hydroxide gradient was employed using two reservoirs of 5 mM and 40 mM NaOH. The optimised gradient profile was as follows: 5 mM hydroxide from 0 to 7.5 min; a linear ramp from 5 to 40 mM hydroxide from 7.5 to 18 min, and maintained at 40 mM hydroxide to 23 min. Equilibration time was 16 min (total time = 39 min). For the identification of unknown species, a Waters Quattro electrospray ionisation-triple quadrupole mass spectrometer was used in negative ion mode (Waters Corporation, MA, USA). Isolated peaks from IC separations were diluted by 50% in MeOH and infused using a syringe pump set at a rate of 0.600  $\mu$ L/h (Cole-Parmer Instrument Co. Ltd., London, UK). All MS conditions can be found in [Supplementary information \(SI, Table S2\)](#).

### 2.3. GSR collection and sample preparation

Twenty-nine cartridges of each of a 0.338" Lapua Magnum (8.6 mm  $\times$  70 mm; Nammo Lapua Oy, Finland), a 0.308" Winchester (7.62 mm  $\times$  51 mm, Winchester Ammunition, Alton, Illinois) a 0.380" Luger Parabellum (9 mm  $\times$  19 mm) were collected separately in sealed polythene bags after firing, stored in the dark at 4 °C and were analysed within 2 weeks. Cartridges were filled with 5 mL, 3 mL and

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