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Rapid Communication

Gunshot residue (GSR) analysis by single particle inductively coupled plasma mass spectrometry (spICP-MS)

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ABSTRACT

Single particle inductively coupled plasma mass spectrometry (spICP-MS) was investigated as a screening-level technique for the analysis and characterization of inorganic gunshot residue (IGSR) nanoparticles. spICP-MS works with undigested samples whereby nanoparticles (NPs) in a suspension are individually atomized and ionized as they reach the plasma, each resulting in a pulse of analyte ions that can be quantified. The method is rapid, and signals from hundreds of NPs can be collected in 1–2 min per sample. The technique is quantitative for NP mass and number concentration when only one element (single element mode) is measured using a quadrupole MS. Likewise, a qualitative elemental fingerprint can be obtained for individual NPs when peak-hopping between two elements (dual element mode). For this proof of concept study, each shooter's hand was sampled with ultrapure water or swab to obtain NPs suspensions. Measurements of antimony, barium, and lead were performed using both analysis modes. With no sample preparation and fully automated sample introduction, it is possible to analyze more than 100 samples in a day. Results show that this technique opens a new perspective for future research on GSR sample identification and characterization and can complement SEM/EDX analysis.

1. Introduction

The discharge of a firearm causes the combustion of the primer and propellant of a cartridge, producing gases that escape through openings of the gun. Gunshot residue (GSR) can be classified as organic (OGSR) or inorganic (IGSR), with their relative importance depending on the type of ammunition. The condensation of these gases produces micro and nanoparticles that make up IGSR. IGSR may or may not contain lead, and the composition of these particles can vary, mainly because of different primer components. Metal-free ammunition, used to minimize the exposure of shooters to toxic metals (primarily at firing ranges), is composed of organic explosives. The burnt and unburnt propellant residues give origin to organic GSR (OGSR) [1,2]. The results presented herein were obtained for IGSR generated from primers containing lead styphnate, barium nitrate and antimony sulfide, which gives a particle composed of lead (Pb), barium (Ba) and antimony (Sb) [3]. Even though there is an increasing use of lead- and metal-free ammunition, most ammunition uses this type of primer [3,4].

The standard method for IGSR casework analysis is Scanning Electron Microscopy (SEM) with Energy-Dispersive X-ray spectroscopy (EDX) [4–7]. However, the setup, analysis, and confirmation of IGSR particles found by the automated search process is tedious and time-consuming. One analysis of a stub can take from two to six hours. In general, with the SEM/EDX method, only a few IGSR particles are detected per sample. The analysis time increases when a sample contains a large number of either identifiable IGSR and/or background particles [3]. Although SEM/EDX will likely remain the only method that is legally-accepted for crime scene investigations, there are reasons to examine alternative approaches. For example, after the discharge of a firearm, GSR particles can be deposited onto the shooter's hands, clothing or other objects and people in the proximity. Thus, the analysis of the spatial distribution of IGSR, which would require a large number of sample analyses, could give insight into the dynamics of events at a crime scene. Similarly, a temporal study of IGSR on surfaces (skin, textiles, etc.), under various environmental conditions, would provide insight into the persistence of IGSR on evidential materials.

According to ASTM [5], particles are classified as: characteristic of IGSR, when they have all 3 elements; consistent with IGSR, when they have 2 of the elements; and commonly associated with IGSR

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when they have only one of the elements. The same ASTM standard states that the presence of commonly-associated particles, in addition to particles that are characteristic of and/or consistent with GSR, can be of significance in the examination of GSR.

Until now, no other available analytical technique could readily give information on the size and elemental composition of each individual particle [1,7–9], making SEM-EDX the only method capable of identifying characteristic GSR particles. In other words, to be considered GSR specific, any alternative method should identify particles having the chemical composition of GSR.

The high sensitivity of ICP-MS makes it a good tool for the analysis of trace metals, but usually it is a bulk [6,7,10] analysis, meaning that the sample has to be digested first. Single particle ICP-MS (spICP-MS) can identify individual, undigested particles and analyze their composition, giving some information on particle morphology (primarily particle size) and number concentration [11]. Because the elements are not to be digested, there are no chemicals involved in sample preparation other than water, although the use of surfactants could be helpful in enhancing IGSR recovery.

Although characteristic IGSR contains three elements of interest, quadrupole based instruments (QMS) generally are used in spICP-MS to only measure one element. Integration of the elemental signal generated by the short transient events that arise from particles can be performed without any data loss by eliminating QMS settling time (ST). Furthermore, collecting data at microsecond dwell times (DT) allows for examination of the peak shape and improves the ability to avoid particle coincidence (two or more particles simultaneously being integrated). These two spICP-QMS parameters are of great importance for the optimization of dual element mode analysis. In this mode the QMS is rapidly jumped back and forth between two elements. Some preliminary spICP-MS studies have indeed shown that QMS can be used to analyze two elements in a NP by utilizing as short as possible ST and DT, on the order of 100 μs or less [12]. DT is the period of time over which ions that impact on the detector are counted. When the time scale is very small, there is a tradeoff between using a short DT, to maximize the number of times a target m/z can be visited, and the detection of the element. With longer DTs the ion counting is greater, but as the QMS switches to the other target m/z and back, and given that the duration of a NP-produced signal is 200–500 μs, the signal of the first m/z might have vanished.

The other parameter, ST, is the amount of time allowed for the electronics of the instrument to switch to the next target m/z measurement state and to stabilize. If the ST is too long, there is a loss of precious time needed to measure the two target m/z as the instrument switches between them. If the ST is not long enough for the instrument to switch and stabilize to the new m/z, the number of ions counted will be smaller than the expected value. This will happen even when the instrument is stabilized to the new m/z but the ions did not have enough time to travel the full length of the quadrupole. A more serious case will be if ST is even shorter and some of the ions from previous m/z reading (DT), which are still in the quadrupole, reach the detector. This results in a false positive contribution of the m/z previously measured to the new m/z being measured. A manuscript describing optimization of DT and ST for dual mode spICP-MS is in preparation.

This dual element approach, applied to samples collected from different individuals after the discharge of a firearm, were used to investigate the suitability of spICP-MS to analyze IGSR.

Though it is not possible to analyze all 3 elements of a characteristic IGSR particle with spICP-QMS, particles consistent with IGSR can be detected. Furthermore, the lack of sample preparation, fast analysis time (1 min), automated post processing and the high number of particles analyzed, make spICP-MS a promising technique to investigate further.

2. Materials and methods

Two GSR sampling techniques were investigated. In both cases samples were collected immediately after one discharge of a firearm, a Taurus PT100 .40 S&W. The ammunition used were CBC .40 S&W full metal jacket. The first method consisted of washing each of the shooters' hand with 50 mL of ultrapure water dispensed from a wash bottle. Formaldehyde (0.2%) was added to the sample in order to avoid fungal growth. Samples were transferred using a pre-cleaned funnel into 50 mL polystyrene tubes. There was no distinction from which part of the hand samples were collected, i.e. whole hand wash, both back and palm, were collected in the same step.

The other approach consisted of swabbing the palm and back of a suspect's hand using cotton swabs dry or wet with ultrapure water. The extraction of particles from the swabs was carried out by putting the swabs in a plastic tube with 10 mL of ultrapure water and sonicating for 2 min in a bath sonicator. After that, the swabs were removed and the samples analyzed. In this case two samples were collected from each hand: one from the palm and one from the back.

The instrument used was a PerkinElmer NexION 300D with a prototype dual element mode Syngystix^{TM} software. spICP-QMS system preparation does not need any special procedure. After the plasma is lit it is left 45 min to stabilize and after that the instrument is tuned according to the manufacture's procedure. After tuning, the quadrupole rod offset (QRO) voltage is set to -20 V in order to increase the velocity of the ions in the quadrupole and reduce the ST needed for the reading of a second element m/z when dual element mode was used. DT was set to 29 μs and the optimum ST was set to 145 μs (publication in prep). For lead isotopes the DT and ST were set to 30 μs and 150 μs, respectively. Single element mode used the same DTs as above. Sample introduction rate was 330 μL per minute, delivered by the ICP-MS peristaltic pump. This potentially allows for 150 analysis of each 50 mL sample using a total analysis time of 1 min.

Samples were analyzed in single and dual element mode for ^{121}Sb, ^{137}Ba, ^{208}Pb, ^{121}Sb & ^{137}Ba, ^{121}Sb & ^{208}Pb and ^{137}Ba & ^{208}Pb. Because every particle that contains lead will have the three major isotopes, a second set of readings was done considering the three major lead isotopes (^{206}Pb, ^{207}Pb and ^{208}Pb), their natural abundance being 24.1, 22.1, and 52.4% respectively.

Data was processed using the R package [13], with an algorithm developed by the first author.

3. Results and discussion

Both sampling techniques gave similar results with respect to particle number and composition. However, the swab technique resulted in less sample for investigative purposes.

During sample introduction, the nebulizer produces a fine mist in which some droplets carry IGSR NPs. With the ICP initially set to read one single element/isotope, continuous data readings are generated by instrumental background counts or counts generated by dissolved ion if there are no NPs entering the instrument. As soon as the ions generated by a NP reaches the detector, the intensity increases to a maximum and then decreases back to the background level. Fig. 1 shows results (raw data) of a nanoparticle containing ^{121}Sb.

When there are dissolved ions in the solution, as well as the NP, background will show some intensity above zero (Fig. 2). Nanoparticles are identified as "outliers" that stand significantly above the background. The contiguous signals that are assigned to a NP-generated peak are integrated and background-subtracted. Thus a particle mass detection limit is established by both the instrument sensitivity and the background noise. An example of these time-resolved NP-generated signals are presented in Fig. 3 for one set of each single and dual element mode analysis of ^{121}Sb, ^{137}Ba and ^{208}Pb.

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