Validation of ICP-MS: Determining Threshold Quantities of Metals Indicative of Gunshot Residue

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Abstract

Gunshot residue (GSR) is commonly identified through the use of the Scanning Electron Microscope (SEM) both elementally and morphologically. Unfortunately, the SEM requires a long period of time for analysis per sample, a considerable disadvantage, given the large volume of GSR kits submitted to agencies. One solution may lie with the Inductively Coupled Plasma Mass Spectrometer (ICP-MS), which quickly identifies and quantifies metal concentrations present in solution for a large number of samples.

This study examined the agreement between ICP-MS and SEM analysis to determine the ideal quantities of metals reported by the ICP-MS that would merit examination by the SEM, as well as the effect time and activity have on the amount and composition of particles. Results suggest additional samples will be required for ideal metal quantities to be determined and that the presences of particles of interest are inversely proportional to both time and activity.

Introduction

Gunshot residue (GSR) is defined as round particles of lead, barium, and antimony (Pb-Ba-Sb). GSR associated particles may be any of the following: round lead particles, (including round lead-barium and round lead-antimony particles), round Ba-Sb particles, and non-round Pb-Ba-Sb particles. These particles are deposited on nearby substrates after a firearm discharges. Once deposited, these particles can then be collected for analysis by swab and/or particle lift. Post collection, instrumental analysis can be performed to identify these particles elementally and morphologically.

Materials and Methods

<u>Materials</u>

- ASPEX® 3025 SEM
- Agilent® 7500cs ICP-MS with ASX-500 Series ICP-MS autosampler
- Ruger® Mark II Target (.22) and ammunition
- Charter Arms® Bulldog Pug (.44) and ammunition
- GSR Kits – made in house

<u>Methods</u>

Participants washed their hands prior to firing the firearms. Each one would load a single round into the magazine or cylinder of the firearm, discharge the firearm toward the target approximately four meters away, and then record the time at which they shot the firearm. Each shooter then returned to his or her daily routine until it was time to collect the GSR.

The shooters' hands were first forcefully dabbed with particle lifts for SEM analysis. Next, swabs from the shooters were collected using 5% nitric acid and cotton swabs for the ICP-MS, which then underwent a filtration step prior to analysis.

Results

The effect of time was examined by comparing the amounts of specific particles from one time interval to the next. The particles in question were GSR particles (round Pb-Ba-Sb particles), round lead particles, and non-round Pb-Ba-Sb particles. The particles were confirmed, morphologically and elementally, by the SEM. A lift lacking confirmed particles was defined as a negative result. Figure 1 illustrates this data graphically

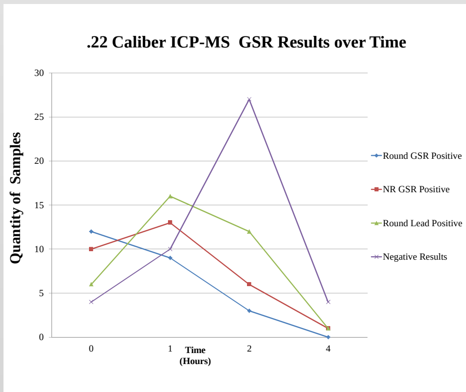

Figure 1. Display of the number of positive identifications of Round GSR, Non-round GSR, and Round Lead, as well as number of Negative results. A steady decline can be observed as time since shooting increases.

- Quantities of lead, barium, and antimony reported by the ICP-MS showed a consistent decrease the course of time.
- As the time interval between firing and collection increased, the number of negatives found increased.

In the samples analyzed, no discernible pattern has emerged in comparing quantities of lead, barium and antimony measured by the ICP-MS as correlative to the presence of round GSR, non-round GSR, or round lead particles confirmed by the SEM. For the 1 hour, .22 samples, quantities of lead, barium and antimony were reported graphically, (Figure 2). Sample statistics were performed, including ANOVA testing (Table 1).

The data sets have been divided into four groups:

- Round GSR positive
- Non-round GSR positive
- Round Pb positive
- Negatives.

All data points were categorized into a group based on what particles were confirmed by SEM analysis for a given sample.

Table 1. F values represent a difference of variance, where P values represent a difference in means. Each category of particle classification was compared by element.

ICP-MS ANOVA Test Results - 22 at One Hour

	Pb	Ba	Sb
F Values	40.9	1.6	0.8
P Value	9.4E-07	0.2	0.5

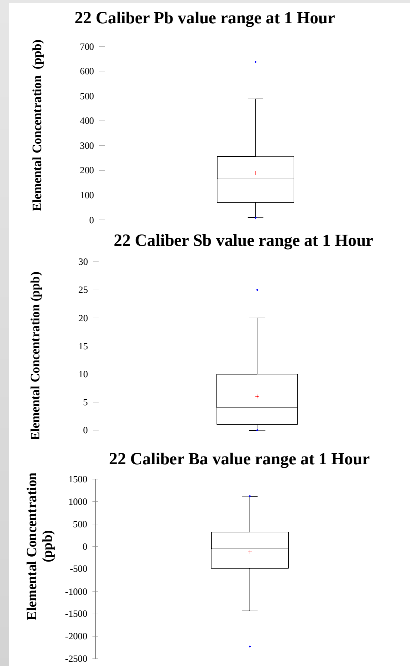

Figure 2. Concentrations of elements detected by ICP-MS using .22 caliber samples at one hour. The samples taken were plotted to display the large range of values found. Red markers indicate the mean, while blue markers represent the minimum and maximum values.

Discussion

- There is a negative correlation between time and the number of particles of each type located.
  - GSR particles exhibit a steady decline in amounts over time.
  - Potential degradation from round GSR to non-round Pb-Ba-Sb may be a cause.

- Lead had sufficient variance and difference of means to be categorized.
- Barium and antimony lacked consistent quantitation values to allow for characterization.
- This behavior seems to have been generated by the significant variance found in the quantitation results.

- Samples confirmed to have GSR/associated particles exhibited a large range of concentrations.
  - Lead had a suspected outlier, concentration of 4287, that was removed from the statistic calculations.

- Large discrepancies in behavior have a number of potential explanations:
- Environmental barium deposition
- Inert variation in skin trace metal concentration.
- Slightly variant amounts of primers in the .22 caliber rounds.

Conclusions

The number of positive results for gunshot residue and associated particles decrease in quantity as the time between firearm discharge and collection increases. Non-round Pb-Ba-Sb particles are more prevalent than round GSR at most time intervals. This is most likely due to a morphology loss by the round GSR, a result of time and activity, to form non-round Pb-Ba-Sb particles.

Given this sample set, no apparent pattern has emerged when correlating trace metal quantities of lead, barium and antimony to positive or negative identifications of gunshot residue. Quantities reported exhibited a large range of possible values, implying a high amount of variance within each individual sample.

Future research would be required to gain more data points for further statistical certainty to this validation. Taking sample blanks from the hands prior to shooting would be another useful step to identify the differences between the skin's natural elemental state and the skin's elemental state after gunshot residue could potentially be deposited. Studies determining the actual amounts of primers found in cartridges would be another pertinent data set to have for this study.

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