THE OCCURRENCE OF FALSE POSITIVE TESTS FOR GUNSHOT RESIDUE BASED ON SIMULATIONS OF THE SUSPECT'S OCCUPATION

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Abstract

Samples collected from high-risk occupations, or simulations thereof, are analyzed for elemental composition using laser-induced breakdown spectroscopy (LIBS) to determine the occurrence of false positive gunshot residue results generated in the work environment. Previous work involving the study of lifetime of detectable amounts of gunshot residue on the hands of a suspect shooter found that gunshot residue exists up to 5.27 days after a firearm discharge. However, certain environmental and/or occupational false positive tests for gunshot residue could result when sampling non-shooters. Samples collected from occupations or simulations thereof include welding, pyrotechnics, key cutting, mechanics, and paper products all of which produced significant false positive results for gunshot residue.

Keywords: Laser-induced breakdown spectroscopy, LIBS; Gunshot Residue, GSR, Forensic analysis

Introduction

Previously, laser-induced breakdown spectroscopy (LIBS) has been shown a viable method for GSR analysis, providing a fast and relatively inexpensive method for detecting gunshot residue on the hands of shooter (1-4). A commercially available LIBS spectrometer is small and potentially field portable, easily mounted into mobile investigative unit. Criminal investigators may use LIBS to determine if a suspect has recently fired a weapon, obtaining results within seconds. Therefore, LIBS could provide necessary presumptive evidence, allowing investigators to obtain a search warrant or prolong a criminal investigation.

In this paper, we investigate the occurrence of situational/occupational based false positive GSR results using LIBS. Often barium is chosen as the analytical marker for determining the presence of GSR on the hands of suspected shooters. However, we realize that barium is ubiquitous, accounting for approximately 0.05% by mass of the earth's crust. "Barium and its compounds are used in oil and gas drilling muds, automotive paints, stabilizers for plastics, case hardening steels, bricks, tiles, lubricating oils, and jet fuel as well as in various types of pesticides. Total U.S. production for 2004 was 532,000 metric tons, a figure that represented 7.3% of world production." (5). Numerous situational and/ or occupational false positive results have been documented in the literature (6-9). Occupations or simulations thereof included in this study are welders, pyrotechnics, key cutters, mechanics, and paper products.

Welders

The high temperature environment of an arc weld plasma allows sputtering of both the base and weld metal materials. Such materials commonly contain trace amounts of ionic compounds (including barium) added as annealing agents. Sputtered materials may be deposited on the welder's hands and falsely identified as GSR (10).

Pyrotechnics

Examples of pyrotechnic materials include fireworks, solid rocket propellants, and black powder, and are defined as mixtures of chemical elements and compounds that are capable of exothermic reactions for the production of heat, light, gas, smoke, or sound (11). Consumer-grade fireworks were investigated. Barium is a major component used in the manufacture of pyrotechnic devices. Therefore, pyrotechnic reaction residues containing barium could bear resemblance to gunshot residue and produce false positive results (6).

Key Cutters

Metallic dust from copper and zinc alloy keys were simulated with a hand-held grinding tool and tested

for the presence of GSR-like signatures.

Mechanics

Mechanics are exposed to various types of metals while working on vehicles. Brake linings, drums, discs and engine wear metals are several possible sources from which mechanics could be exposed to barium. Particles originating from these wear metals contain barium and could produce emission spectra similar to gunshot residue (7).

Paper Products

Barium Sulfate is used as a base for water color pigment and as a filler in manufacturer of paper products (5). Therefore, there exists the potential for workers to become contaminated with higher levels of barium in the manufacturing process, shredding and recycling centers, etc.

Experimental

Samples were collected using 3M 5490 PTFE (3M Corp., St. Paul, MN) extruded film tape (chosen for its low emission background) (2) pressed into the webbing of the shooter's hand. Multiple tape contacts were used to obtain residue from the first knuckle of the trigger finger, through the webbing between the thumb and the trigger finger, and around to the first knuckle of the thumb. This area of the hand was chosen for the highest concentration of residues based on the results of comprehensive studies on the formation of the plume of vapors exiting firearms (12). Advantages of the adhesive tape lift technique include: decrease sample preparation and collection time, reduced risk of sample loss, and expanded long term storage properties for future analysis after collection (13). Next, samples are pressed flat and loaded into an OOI LIBS 2000+ Spectrometer (Ocean Optics, Inc. Dunedin, FL) coupled to a Big Sky Ultra 50 mJ Nd:YAG laser (Quantel USA, formerly Big Sky Laser Technologies, Bozeman, MT). Experimental parameters are provided in detail elsewhere (3-4). Representative emission spectra are presented in Figure 1.

Threshold values for a positive GSR test were determined by comparison to a blank library. Twenty five volunteers, known to be free of GSR, were sampled for compilation of a library representing the blank population and analyzed for the presence of emission at Ba(II) 455.403 nm. Twenty laser pulses were taken from each subject's sample giving 500 spectra in the blank library. Each laser pulse sampled a unique location on the sample tape using a 4 x 5 raster pattern to ensure sampling of the top adhesive layer only. The average and standard deviation from the blank samples were used for determination of a threshold value at the Ba (II) 455.403 nm wavelength using Equation 1

$$y_{dl} = \bar{x}_{bl} + 3s_{bl} \quad (1)$$

where y_{dl} is the signal detection limit or "smallest instrument response to sample that is *significantly different* from that of a blank," $\bar{x}_{bl}$ is the mean emission of the blank population, and s_{bl} is standard deviation of the blank population (14). Therefore, calculation of y_{dl} is based on population statistics of the blank library and is independent of the amount of GSR on the hands of a shooter. The signal detection limit defines the threshold value three times the standard deviation of the blank library emission and represents the value that is statistically different from the blank. Values less than y_{dl} fall into the blank population and are said to be naturally occurring whereas values greater than y_{dl} rarely occur in a random population of non-shooters and represent a statistically significant difference. Results are categorized using the following definitions:

A false positive test for GSR was defined when a sample from a non-shooter produced emission signal minus background values greater than the calculated signal detection limit.

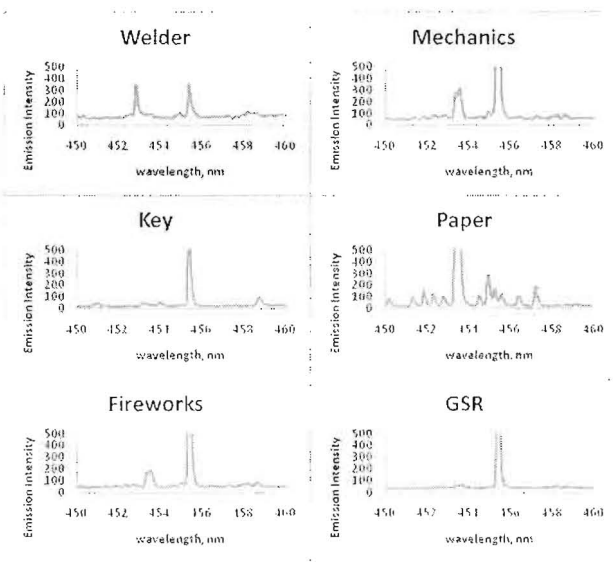

Figure 1. Representative spectra from each occupation/ simulation showing positive/false-positive results for gunshot residue.

A true negative test for GSR was defined when a sample from a non-shooter produced emission signal minus background values less than the calculated signal detection limit.

A true positive test for GSR was defined when a sample from a shooter produced emission signal minus background values greater than the calculated signal detection limit.

A false negative test for GSR was defined when a sample from a shooter produced emission signal minus background values less than the calculated signal detection limit.

Welding samples were collected from an industrial welder after using a Millermatic 251 MIG (metal inert gas) welder (Miller, Appelton, WI). To simulate a pyrotechnician packing explosives into a container, volunteers handled the powder and packaging from commercially available fireworks variety pack (TNT Fireworks, Florence, AL). To simulate the grinding wheel mechanism used to cut new keys commercially, keys were cut by hand with a Dremel rotary tool (Dremel, Mt. Prospect IL). Samples were collected from a working mechanic after completing a routine shift in which, the mechanic was instructed to perform normal tasks (including hand washings). Paper products were shredded in a commercially available paper shredder and volunteers were asked to use their bare hands to transfer the shredded paper to the waste bin. Samples from all occupations or simulations thereof were collected on 3M 5490 PTFE extruded film tape and analyzed by LIBS following the experimental procedures for the blank population above.

Results and Discussion

All tested occupations and/or simulations produced significant false positive results for gunshot residue (Table 1). Pyrotechnic simulations produced the highest false positive results with a value of 95%. We hypothesized that pyrotechnic occupation would yield the highest false positive result because of the similarity of the major components found in both fireworks and ammunition primers. The spattering of weld metals, including trace amounts of barium contributed to the observed increase levels of barium thus causing an 80% of false positive result for gunshot residue. Mechanics produced the third highest error rates at 69% likely due to the occupational contact with wear metals and brake dust containing barium. Although, relatively small in comparison with the other high-risk occupational results, paper products and key cutter simulations did produce false positive results of 32% and 17%, respectively. Particles of gunshot residue are inherently heterogeneous and will be randomly distributed about the shooter's hand and subsequently, the collection tape. Therefore, individual LIBS spectra taken from samples collected from an actual shooter may produce false negative results (2-3). In the future, the multi-element nature of LIBS may be used to determine the presence of other metals, specific to each occupation, and not originating from a firearm discharge, thus excluding them from the GSR library.

Table 1. Summary of Gunshot Residue Results Based on Suspects' Occupation/Simulation.

Occupation/ Simulation	Number of Individual LIBS Spectra	% False Positive For GSR	% True Negative
Welder	40	80%	20%
Mechanic	100	69%	31%
Key Cutter	105	17%	83%
Paper	50	32%	68%
Fireworks	100	95%	5%
		% True Positive For GSR	% False Negative
Gunshot Residue	68	90%	10%

Conclusion

False positive results, collected from non-shooters, for gunshot residue were detected in every occupation/ simulation tested. Inclusion of high-risk occupations into the LIBS library may be necessary to avoid the high occurrence of false-positive results. However, these will likely results in an increase in the decision threshold limit; thus increasing the occurrence of false negative errors in the detection of GSR produced from a suspect shooter. In the future, the multi-element nature of LIBS may be used to determine the presence of other metals, specific to each occupation, and not originating from a firearm discharge.

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