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Gunshot Residue Analysis in the Undergraduate Laboratory Using Toy Cap Guns

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ABSTRACT The authors developed an experiment for the undergraduate analytical or forensic chemistry laboratory in which gunshot residues (GSRs) produced from toy cap guns are analyzed by laser-induced breakdown spectroscopy (LIBS). Alternatively, the experiment is readily adaptable to any emission spectroscopy technique. This project allows students to investigate the development of a forensic method while addressing proper sampling techniques used in forensic investigations. Students were able to develop a library of blank samples, establish signal detection limits to address legal considerations for determination of false-positive and -negative error rates, and optimize an emission spectrometer.

KEYWORDS forensic analysis, GSR, gunshot residue, laser-induced breakdown spectroscopy, LIBS, spectroscopy education

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INTRODUCTION

There is a documented need for experiments addressing so-called "real sampling" in chemical education.[1–2] In traditional laboratory manuals, students fall into a routine of solving quantitative analyses on clean analytical samples prepared by teaching staff in the stockroom. "Students learn to believe that for every analytical problem there is a 'right number,' and the sole purpose of analysis is to produce it."[1] Previous publications have established that the analysis of gunshot residues (GSRs) provides an excellent framework for teaching sampling and statistical analyses.[1–2] Rather than solving for a right or wrong answer, students must generate threshold values for positive GSR tests by comparing results with a library of blank samples presumed to be free of GSR. Bulk analysis techniques often rely on the generation of a hand-blank database to report the naturally occurring background level of the GSR and other metals on skin. Once threshold values have been established, positive or negative results can be assigned by comparison to the statistical population in the library of blank volunteers. Careful use of the hand-blank library is crucial to the success of established bulk analysis techniques.[3–5] Furthermore, the analysis of GSR as a

situational context can "provide motivation for performing the experiment so as to maintain or pique the students' interests."[2]

Harrison and Gilroy published the first presumptive test for the inorganic components of GSR in 1959.[6] In their experiment, reagents are added in sequence to test for the presence of barium, lead, and antimony. Most GSR particles are approximately 20–40 μm in diameter and are uniquely composed of Ba, Pb, and Sb such that the presence of these three elements remains the basis of modern forensic GSR analysis.[7–9] Numerous instrumental methods have proven viable for GSR analysis. These include scanning electron microscopy with an energy dispersive X-ray spectrometry (SEM-EDX),[9,10] atomic absorption spectroscopy (AAS),[1,2] Fourier transform infrared attenuated total reflectance (FTIR/ATR),[11] and the more recent laser induced breakdown spectroscopy (LIBS).[3–5] However, few examples of the analysis of GSR exist in the chemical education literature. Previous publications describe sampling for barium, lead, and/or antimony by firing primers in starter pistols,[2] taking field trips to sample law enforcement officers,[1] or staging samples that mimic firearms discharge.[12] Analysis techniques on these samples include electrothermal atomization–atomic absorption spectroscopy (ETAAS),[1,2] flame atomic absorption spectroscopy (FAAS),[12] and presumptive microchemical testing by colorimetric assay.[12]

We propose, for the first time, the novel use of toy cap guns as a simulant for GSR. When the toy cap gun is fired, the firing pin strikes the ammunition cap and ignites the pyrotechnic material (potassium chlorate). Openings in the gun allow residues to escape into the air where they are distributed on the shooters hands and clothing. Samples are then analyzed by atomic emission spectroscopy, and the resulting spectra are used to identify atomic and ionic emission lines characteristic of the pyrotechnic material (i.e., K(I) 766.490 nm and K(I) 769.896 nm). Using the emission spectra, students develop a library of blank samples, establish signal detection limits to address legal considerations for determination of false-positive and -negative error rates, and optimize an emission spectrometer.

Students collect their own samples using toy cap guns and then analyze those samples by atomic emission spectroscopy. This gives students the opportunity to develop an analytical method and

then use their data to define the threshold for positive and negative results, thus reinforcing the fact that not every analytical scenario must have a single right answer. Additionally, numerous articles in primary literature,[3–5] popular science magazines,[13,14] and common textbooks[15,16] provide significant background to allow students to research the literature to provide new variables to investigate at the end of the laboratory period. For example, students in our classes have provided samples to begin investigating sources of occupational false-positive contamination,[17–19] the HILTI® defense (primer-based industrial construction tools),[13] and statistical comparisons of the amount of GSR produced by different regions of the gun (barrel, handle, chamber).

MATERIALS AND METHODS

GSR is produced by firing rounds from a die-cast frame of a Sterling replica Cowboy series cap pistol loaded with 2.20-grain ring-cap 8-shot (single card) ammunition caps (gun and caps made in Taiwan). The ingredients listed for the ammunition caps included potassium chlorate, red phosphorous, sand, and glue. Samples were collected using 3 M 5490 PTFE (3 M Corp., St. Paul, MN) extruded film tape (chosen for its low-emission background) pressed into the webbing of the shooter's hand.[4] 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 a comprehensive plume study performed by Schwoeble and Exline.[8] 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.[20] 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). A representative emission spectrum from a positive GSR sample is presented in Fig. 1. Major emission lines include Ca(II) 393.366 nm, Ca(II) 396.847, Ca(I) 422.673 nm, Na(I) 588.995 nm, Na(I) 589.592 nm, Hα 656.2 nm, K(I) 766.490 nm, K(I) 769.896 nm, and
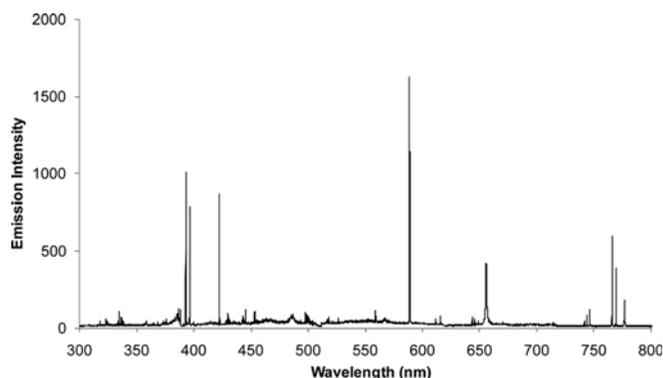
Gunshot Residue Analysis

FIGURE 1 Representative emission spectrum from a positive GSR sample. Major emission lines include Ca(II) 393.366 nm, Ca(II) 396.847, Ca(I) 422.673 nm, Na(I) 588.995 nm, Na(I) 589.592 nm, Hα 656.2 nm, K(I) 766.490 nm, K(I) 769.896 nm, and O(I) 777.194 nm.

O(I) 777.194 nm. Alternatively, the experiment is readily adaptable to any emission spectroscopy technique.

Threshold values for a positive GSR test were determined by comparison with a blank library. We sampled 25 volunteers, known to be free of GSR, for compilation of the population blank library and analyzed them for the presence of GSR. We took 20 laser pulses from each subject's sample, yielding 500 spectra in the blank library. Each laser pulse sampled a unique location on the sample tape using a 4×5 raster pattern to ensure sampling of the top adhesive layer only. Potassium (from the potassium chlorate in the ammunition caps) was chosen as the analytical marker for determining the presence of GSR on the hands of suspected shooters. The average and standard deviation from the blank samples were used for determination of a threshold value at the K(I) 766.490-nm and K(I) 769.896-nm wavelengths using Eq. (1),

$$y_{dl} = \bar{x}_{bl} + 3s_{bl} \tag{1}$$

where y_{dl} is the signal detection limit or "smallest instrument response to sample that is *significantly different* from that of a blank,"[16] $\bar{x}_{bl}$ is the mean emission of the blank population, and s_x is standard deviation of the blank population.[16] 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 significant difference within the 99% level of confidence.

RESULTS AND DISCUSSION

Students collected samples from the hands of their group members after firing the cap guns. These samples are labeled as "suspect" in an effort to determine who in the class had fired the weapon. Additional student-generated samples were collected as controls and tested at random during the cap gun experiments to diagnose false-positive errors and further validate method performance. Positive controls were tested in two ways: first by sampling the un-reacted grains of pyrotechnic material, and second by directly sampling residues from the chamber of the cap gun. Negative controls were taken from volunteers who had not handled the cap guns or pyrotechnic material in the past 24 hr to diagnose the possibility of false-positive errors. Using Eq. (1), and the 500 spectra in the blank library, we found that the signal detection limits (y_{dl}) or threshold values at the K(I) 766.490-nm and K(I) 769.896-nm wavelengths were 285.1 and 215.6 emission intensity units respectively.

We sampled 50 negative controls from non-shooters, yielding an average K(I) 766.490-nm emission of 51.1 ± 30.8 units and K(I) 769.896-nm emission of 36.3 ± 22.7 units. Those values were well below the signal detection limits (285.1 and 215.6 units). The relatively large emission intensities and standard deviations are explained by the naturally occurring background contamination of potassium on skin, which produces a normal or Gaussian distribution. Figure 2 shows the differences in emission intensities when comparing a positive control GSR sample originating from the potassium chlorate in the toy cap gun and a negative control sample taken from a blank volunteer. Therefore, in Fig. 2, the positive sample contains levels of potassium that are statistically significantly different from those of the blank population, while the negative sample contains levels of potassium that are similar to those of the blank population. Students examine
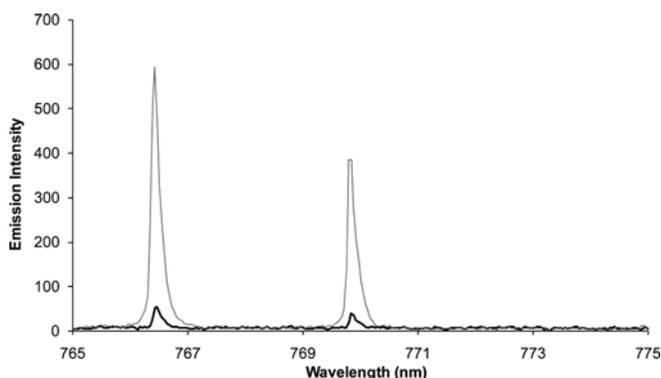
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FIGURE 2 (▨) Representative emission spectrum from a positive GSR sample at K(I) 766.490-nm and K(I) 769.896-nm wavelengths originating from the potassium chlorate in the toy cap gun and (■) a sample taken from a blank volunteer.

the emission intensities, compare the individual spectrum to the signal detection threshold, and categorize the sample as one of the following:

1. *A true positive* test for GSR was defined when a sample from a shooter produced values of emission signal minus background greater than the calculated signal detection limit for both K wavelengths.
2. *A false-positive* test for GSR was defined when a sample from a non-shooter produced values of emission signal minus background greater than the calculated signal detection limit for both K wavelengths.
3. *A true negative* test for GSR was defined when a sample from a non-shooter produced values of emission signal minus background less than the calculated signal detection limit for either of the K wavelengths.
4. *A false-negative* test for GSR was defined when a sample from a shooter produced values of emission signal minus background less than the calculated signal detection limit for either of the K wavelengths.

By grouping each student-generated spectrum into one of these four categories, students begin to

define error rates for their new forensic analytical method, a requirement for admissibility of scientific techniques by *Daubert v. Merrell Dow Pharmaceuticals, 509 U.S. 579 (1993)*. Table 1 summarizes the student-generated data. Negative controls (non-shooters) produce 100% negative and no false-positive results. However, the positive controls (grains of pyrotechnic material) produce only 94% positive results and 6% false-negative results. The positive controls from the chamber of the cap gun produce results similar to those of the population of suspect shooters. The high error rates in Table 1 (63% false negative for shooters and 54% false negative for positive controls from the cap gun chamber) result from the fact that potassium as an analytical marker is non-specific to GSR. Students easily justify their data through the background literature, and most students realize that potassium is ubiquitous, accounting for approximately 1.5% (by mass) of the earth's crust.

CONCLUSIONS

Analysis of toy cap gun residues can serve as an excellent introduction to atomic emission spectroscopy using LIBS and could easily be modified to be performed on inductively coupled plasma (ICP) or flame atomic emission spectroscopy (FAES), in which case emission intensity units can be calibrated to a concentration of potassium. For example, ICP data from our lab show an absolute mass of 34.43 ± 9.90-µg K recovered from dilute nitric acid swabs of a population of non-shooters and 78.67 ± 27.37-µg K for a population of shooters, n = 15. The data analysis also reinforces concepts from popular analytical and forensic textbooks that include chapters on statistical analysis of laboratory data, and interpretation of the statistical analysis provides excellent opportunities for supplementing the laboratory exercise or lecture instruction with further discussion of the concepts of *acceptable margin of error* and *beyond a reasonable doubt*. In this

TABLE 1 Using the Signal Detection Limit as a Decision Threshold, Students Define False-Positive and False-Negative Error Rates for the Analysis of GSR by LIBS

Sample type	n	% Positive	% False negative	% Negative	% False positive
Suspects (Shooters)	200	34	63	–	–
Negative Control (Non shooters)	50	–	–	100	0
Positive Control (pyrotechnic grains)	50	94	6	–	–
Positive Control (gun chamber)	50	46	54	–	–

experiment, the large positive and negative error rates arise from the natural environmental background levels of potassium on skin and are not normally present when analyzing actual bullet GSRs, which contains Ba, Pb, and Sb. However, student feedback has been very favorable. We believe that any shortcomings in the quality of the data (high error rates) are outweighed by the hands-on experiences allowing students to develop a library of blank samples, establish signal detection limits to address legal considerations for determination of false-positive and -negative error rates, and optimize an emission spectrometer.

ACKNOWLEDGMENTS

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