Determining the Lifetime of Detectable Amounts of Gunshot Residue on the Hands of a Shooter Using Laser-Induced Breakdown Spectroscopy

MATTHEW B. ROSENBERG and CHRISTOPHER R. DOCKERY*

Department of Chemistry and Biochemistry, Kennesaw State University, 1000 Chastain Road, Kennesaw, Georgia 30144

Laser-induced breakdown spectroscopy (LIBS) has been used to determine the period of time that a shooter will test positive for gunshot residue (GSR) after firing a revolver. Multiple rounds of primer were fired and samples collected at multiple hour intervals using an adhesive tape pressed against the skin. Samples were analyzed directly using a commercially available laser-induced breakdown spectrometer where barium emission (originating from barium nitrate in the primer) was observed. Population statistics were used to compare suspected GSR to a library of blank samples from which a threshold value was established. Statistically significant results, positive for GSR, are obtained 5.27 days after a firearm discharge using these techniques.

Index Headings: **Laser-induced breakdown spectroscopy; LIBS; Gunshot residue; GSR; Forensic analysis.**

INTRODUCTION

Ammunition cartridges are made of four major components: (1) a bullet usually made from lead jacketed with copper, (2) a shell casing usually made from brass, (3) a propellant composed of nitrocellulose and nitroglycerine, and (4) a primer cap, which contains a primary explosive, a fuel, and an oxidant. Nearly all primer caps contain lead styphnate primary explosive, antimony sulfide fuel, and barium nitrate oxidant.[1] Few exceptions including Chinese and Russian ammunition use different mixtures in the primer cap, such as a mercury fulminate primary explosive.[2] When a firearm is discharged, the firing pin strikes the primer and ignites the propellant. The propellant then burns and the resulting vapors expand, creating pressure to force the bullet down the barrel of the gun. Residual particles can vaporize in the high-temperature and -pressure environment of a firearm discharge. Openings in a firearm allow these vapors to escape into the air as an expansion plume, where they quickly cool and form the particulate matter known as gunshot residue (GSR). The majority of GSR formed during a firearm discharge is released from openings in the weapon that include the breeches (e.g., cylinder gap of a revolver).[3] As the expansion plume cools and expands, residues may be deposited on the hands, face, clothing, objects in the vicinity, and vehicles.[1] Forensic analyses, both presumptive and confirmative, have been developed for the organic and inorganic components of gunshot residue.

Previous field portable or presumptive tests used to detect gunshot residues are based on visualization of colorimetric assays. The dermal nitrate test created in the 1930s uses a 0.25% solution of N,N′-diphenyl-benzidine, which turns blue when GSR is present. However, this test is not selective and responds to all organic compounds containing the nitro-functional group. Numerous false positive results exist from materials such as blood, urine, fertilizers, etc.[4] Harrison and Gilroy published the first presumptive test for the inorganic components of GSR in 1959.[5] 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.

Accurate determination of the lifetime of detectable amounts of GSR on the hands of a shooter is important to the forensic analyst. If GSR could be detected over a period of several days, then GSR collected from a shooter's hands or clothing could be connected to a firearm discharge preceding a criminal investigation.[6] It is accepted that the persistence of GSR on the hands of a shooter decreases with time. Estimates for the period of time GSR remains on the hands of a shooter vary in the literature between 1 and 48 hours.[1,4,6–9] However, the inorganic components of GSR "can last in a normal environment indefinitely."[1] Therefore, GSR particles embedded into the skin during firearm discharge could remain on the skin cells until they desquamate, a process which takes place approximately every 4 weeks.[10,11] Normal daily conditions including hand washings[4,6,9] and other physical activity[1] including rubbing hands against materials (towels, clothing, etc.) or putting hands in pockets or handcuffing them behind the back[7] could accelerate this process. GSR that remains on a shooter's hands after washing may depend on the frequency and nature of the washings.[12] In some cases, it has been suggested that GSR collected from the face, hair, and clothing may remain longer after a firearm discharge when compared to sampling the shooter's hands.[13]

Examination of gunshot residue has traditionally been performed by scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) using the tape-lift method for sample collection. SEM-EDS has the ability to determine the composition of elements of individual particles of GSR based on the interaction of the elements with the high-energy radiation of an electron beam. If the scanning-electron microscope finds a single particle that has morphology consistent with GSR and contains Ba, Pb, and Sb, the particle is unambiguously identified as having originated from a firearm discharge. Similar particles that contain only two of the three components are classified as characteristic of GSR.[1,4,5,14]

Previously, laser-induced breakdown spectroscopy (LIBS) has been shown to be a viable method for GSR analysis.[5] While LIBS cannot replace the unambiguous nature of the "unique" GSR particle, it may provide a fast and relatively inexpensive method for detecting gunshot residue on the hands of a shooter. We envision the LIBS technique as complementary to SEM-EDS, where LIBS combines the selectivity of

Received 22 May 2008; accepted 5 August 2008.
* Author to whom correspondence should be sent. E-mail: cdockery@kennesaw.edu.

0003-7028/08/6211-1238$2.00/0

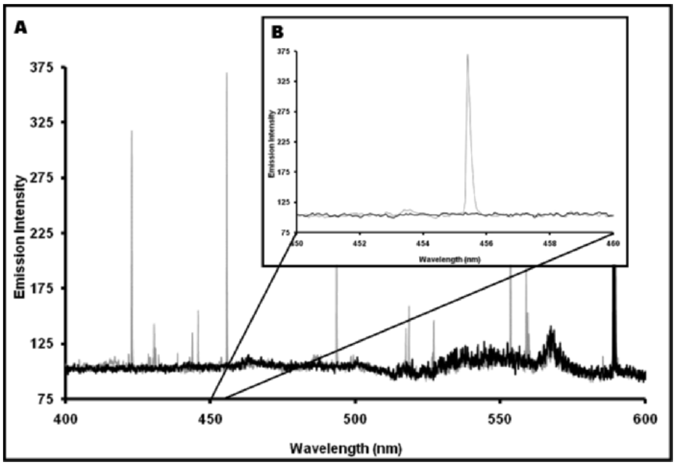

FIG. 1. (**A**) (Black line) Sample taken from a volunteer who is known to be free of gunshot residue overlaid with (gray line) a positive GSR test 72 hours after firearm discharge. (**B**) Barium (II) emission at 455.403 nm used as the analytical wavelength for (black line) sample taken from a volunteer who is known to be free of gunshot residue and (gray line) a positive GSR test 72 hours after firearm discharge.

multielement analysis and the sensitivity of modern instrumental techniques into a presumptive field test and SEM-EDS remains the "gold standard" for confirmatory testing of GSR. A commercially available LIBS spectrometer is small and potentially field portable, easily mounted into a mobile investigative unit. Criminal investigators may use LIBS to determine whether 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. The scope of this paper is to provide investigators with a time frame for determining detectable amounts of gunshot residue on the hands of a shooter while using LIBS as a potential field-portable or presumptive test for gunshot residue.

EXPERIMENTAL

A .357 caliber Colt Trooper MK III revolver (Colt's Manufacturing Company LLC, Hartford, CT) was used to produce gunshot residue. Empty shell casings were loaded by hand with a large magnum Winchester primer (U.S. Repeating Arms Company, New Haven, CT) using Rock Chuck Bullet Swage (RCBS, Oroville, CA), a type of commercially available ammunition reloading equipment. Samples were collected using 3M 5490 PTFE (3M Corp., St. Paul, MN) extruded film tape (chosen for its low emission background) pressed into the webbing of the shooter's hand.[5] 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 plume studies performed by Schwoeble and Exline.[1] Advantages of the adhesive tape lift technique include decreased sample preparation and collection time, reduced risk of sample loss, and expanded long term storage properties for future analysis after collection.[15] 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).

Threshold values for a positive gunshot residue test were determined by comparison to a blank library. Bulk analysis techniques rely on the generation of a hand-blank database to report the naturally occurring background level of the GSR 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 such as flame atomic and inductively coupled plasma spectroscopy.[5]

Twenty-five volunteers, known to be free of gunshot residues, were sampled for compilation of the population blank library and analyzed for the presence of GSR. Twenty laser pulses were taken from each subject, giving 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. The average and standard deviation from the blank samples were used for determination of a threshold value at the barium (II) 455.403 nm wavelength using Eq. 1:

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

where y_{dl} is the signal detection limit or "smallest instrument response to sample that is *significantly different* from that of a blank," $\bar{x}_{bl}$ 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 where values greater than y_{dl} cannot occur in a random population of non-shooters and represent a significant difference within the 99% level of confidence. Samples were tested as controls and collected at random during the firearm experiments to diagnose false positive errors and further validate method performance. For example, three control samples (60 laser pulses) gave an average Ba (II) 455.403 nm emission of 5.2 units $\pm$ 4.2, well below the signal detection limit of 19.3.

Six shots of large magnum Winchester primer were fired for each replicate experiment and tape-lift samples were collected from one of three volunteer shooters. Each data point represents a unique experiment rather than a continuation in time such that a gun was fired and a sample collected 24 hours later. Then, the volunteers were instructed to wait one week before starting a new experiment where a new firearm discharge would start the clock on a new, independent measurement. In this way, the act of sampling the hand did not modify the amount of GSR present for subsequent experiments. The shooters were instructed to continue normal daily activities including hand washing, bathing, and other physical activities. Emission lines indicative of GSR were observed and recorded for statistical analysis. Figure 1A represents a sample taken from a volunteer known to be free of gunshot residue overlaid with a spectrum taken from a shooter 72 hours after firearm discharge. Lead emission was observed in some experiments, but antimony was not detected due to the fact that the most intense emission lines are in the UV region

TABLE I. Occurrence of positive and negative GSR results at different time intervals using a heterogeneous model where a positive test for gunshot residue was defined when the barium 455.403 nm emission line produced signal minus background values greater than the calculated signal detection limit ($y_{dl} = 19.3$) at *any* location along the sample tape.

Time in hours (days)	Trial 1	Trial 2	Trial 3
12 (0.5)	+	+	+
24 (1.0)	+	+	+
36 (1.5)	+	+	+
48 (2.0)	+	+	+
60 (2.5)	+	+	+
72 (3.0)	+	+	+
96 (4.0)	+	+	+
120 (5)	+	+	+
144 (6)	+	−	+
168 (7)	−	+	−
192 (8)	+	+	+

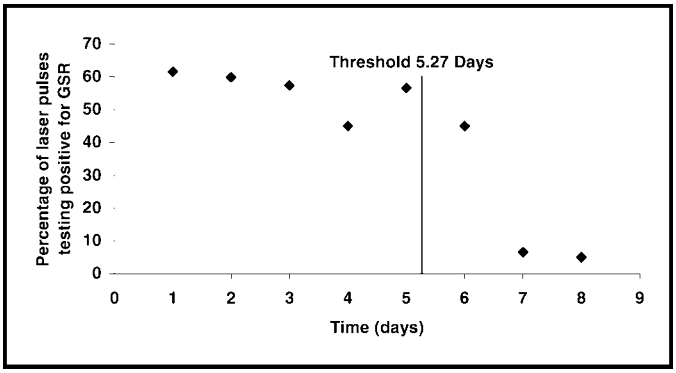

FIG. 2. Percentage of laser pulses testing positive for GSR over time. Individual laser pulses produce positive results up to 192 hours after a firearm discharge due to the heterogeneous nature of GSR.

and are truncated by the fiber-optic cable. Barium was chosen as the analytical probe because there are several strong emission lines in the visible spectrum identified to be free from spectroscopic interferences.[5] Specifically, barium (II) emission at 455.403 nm[17] (shown in Fig. 1B) was used as the analytical wavelength for all subsequent experiments.

RESULTS AND DISCUSSION

Particles of gunshot residue are inherently heterogeneous and will be randomly distributed about the shooter's hand and, subsequently, the collection tape. Spectroscopic averaging dilutes the GSR signal and increases the signal-to-noise ratio.[5] For this reason, a positive test for gunshot residue was defined when the barium 455.403 nm emission line produced signal minus background emission values greater than the calculated signal detection limit ($y_{dl} = 19.3$) at *any* location along the sample tape. Results from this data treatment are presented in Table I and suggest that detectable amounts of GSR on the hands of a shooter are inconsistent approximately 120 hours after a firearm discharge. However, as can be seen in Fig. 2, individual laser pulses may still produce positive results up to 192 hours after a firearm discharge due to the heterogeneous nature of GSR. Therefore, it becomes necessary to fit a quantitative model to the data to determine a more concrete threshold for the lifetime of detectable amounts of GSR on skin.

To quantify the lifetime, an exponential decay model was fit to the data. In doing so, the averages of replicate laser pulses for the multi-hour time intervals were taken. Averaging the heterogeneous matrix dilutes the Ba emission signal and increases the variability in the data. However, we believe that this model provides the forensic chemist with a conservative and reproducible estimate of the detectable lifetime of GSR on skin. Results from the exponential decay model (presented in Fig. 3) show that detectable amounts of GSR are obtained up to 126 hours or 5.27 days after a firearm discharge. After 126 hours, individual laser pulses pass due to the heterogeneous nature of GSR while the exponential decay model fails due to sample averaging and approximating the matrix as homogenous.

Many authors acknowledge that "it is difficult to generalize the period over which residues are retained"[6] and that the lifetime of detectable amounts of GSR depends greatly on both the experimental conditions and the specific instrumental technique.[1,6,7] However, few systematic studies exist that probe the lifetime of inorganic GSR on the hands of a shooter. It has been noted that the number of particles uniquely identified as GSR (containing Ba, Pb, and Sb detected by SEM-EDS) decreases an order of magnitude one hour after a shooting[4] and that antimony and barium decrease substantially after two hours.[6] Jalanti et al. report irreproducibility in GSR particle count and loss of "unique" particles after 2–4 hours.[7] To the best of our knowledge, we present the only systematic study of the bulk analysis of inorganic GSR lifetimes. Using population statistics to define decision thresholds, we remove the requirement of locating and identifying single particles containing Ba, Pb, and Sb, thus allowing longer timeframes for forensically relevant sampling. We are confident in our estimate; up to five days following a firearm discharge, GSR is detectable on the hands of a shooter using this methodology.

CONCLUSION

Threshold values for a positive gunshot residue test were determined by comparison to a blank library composed from twenty five volunteers known to be free of gunshot residue. Samples collected following a firearm discharge systematically produce emission greater than the signal detection limit and we

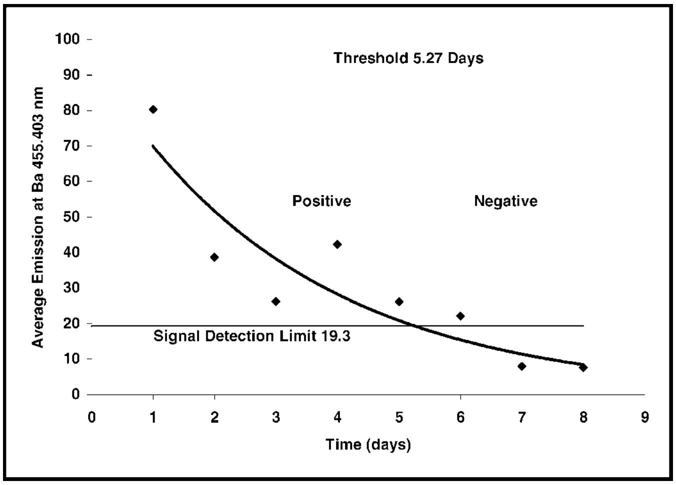

FIG. 3. Exponential decay model of GSR on the hands of a shooter; $y = 94.568e^{-0.3018x}$, $R^2 = 0.8397$. With this model, the lifetime of detectable amounts of GSR is estimated at 5.27 days after a firearm discharge.

are currently able to show a conservative measure of the lifetime for positive gunshot residue results at 126 hours or 5.27 days after a shooting. We are currently evaluating the effect of excessive hand washing and/or other methods used by a shooter attempting to remove gunshot residue from the hands. We are currently investigating published reports of situational/occupational based false positive GSR results such as pyrotechnicians,[18] mechanics,[19] key cutters, and operators of primer-cartridge-based industrial tools.[20]

ACKNOWLEDGMENTS

This work was supported in part by the Department of Chemistry and Biochemistry at Kennesaw State University, a Kennesaw State University-Center for Excellence in Teaching and Learning-Creative Activities and Research Experiences for Teams (CETL-CARET) Grant, and by Ocean Optics, Inc., Innovations in Educational Spectroscopy Grant.

1. A. J. Schwoeble and D. L. Exline, *Forensic Gunshot Residue Analysis* (CRC Press, Boca Raton, FL, 2000).
2. A. Zeichner, N. Levin, and M. Dvorachek, J. Forensic Sci. **37,** 1567 (1992).
3. S. Basu, C. E. Boone, D. J. Denio, and R. A. Miazga, J. Forensic Sci. **42,** 571 (1997).
4. F. S. Romolo and P. Margot, Forensic Sci. Int. **119,** 195 (2001).
5. C. R. Dockery and S. R. Goode, Appl. Opt. **42,** 6153 (2003).
6. H. H. Meng and B. Caddy, J. Forensic Sci. **42,** 553 (1997).
7. T. Jalanti, P. Henchoz, A. Gallusser, and M. S. Bonfanti, Sci. and Just. **39,** 48 (1999).
8. D. M. Norhtrop, J. Forensic Sci. **46,** 560 (2001).
9. Z. Wu, Y. Tong, J. Yu, X. Zhang, C. Yang, C. Pan, X. Y. Deng, Y. X. Wen, and Y. C. Xu, J. Forensic Sci. **46,** 495 (2001).
10. N. A. Campbell and J. B. Reece, *Biology* (Pearson Education Inc., San Francisco, CA, 2005), 7th ed., p. 835.
11. S. Parker, *The Human Body Book* (DK Publishing, Inc., New York, NY, 2007), p. 146.
12. D. G. Havekost, C. A. Peters, and R. D. Koons, J. Forensic Sci. **35,** 1096 (1990).
13. Z. Brozek-Mucha, Z. Zagadnien Nauk Sadowych **41,** 62 (2000).
14. L. Garofano, M. Capra, F. Ferrari, G. P. Bizzaro, D. Di Tullio, M. Dell'Olio, and A. Ghitti, Forensic Sci. Int. **103,** 1 (1999).
15. H. A. Wrobel, J. J. Millar, and M. Kijek, J. Forensic Sci. **43,** 178 (1998).
16. D. C. Harris, *Quantitative Chemical Analysis* (W.H. Freeman and Company, New York, 2007), 7th ed., p. 726.
17. National Institute of Standards and Technology, <http://physics.nist.gov/PhysRefData/ASD/lines_form.html> (2007).
18. P. V. Mosher, M. J. McVicar, E. D. Randall, and E. H Sild, Can. Soc. Forensic Sci. J. **31,** 157 (1998).
19. C. Torre, G. Mattutino, V. Vasino, and C. Robino, J. Forensic Sci. **47,** 494 (2002).
20. J. S. Wallace and J. McQuillan, J. Forensic Sci. Soc. **24,** 495 (1984).