Laser-induced breakdown spectroscopy for the detection of gunshot residues on the hands of a shooter

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Laser-induced breakdown spectroscopy (LIBS) has been used to determine whether the hands of a suspected gun user contain traces of gunshot residue. Samples are obtained by pressing adhesive tape against the skin of the suspect and analyzing the tape directly. When the suspect has fired multiple shots, or if the gun has not been cleaned, the gunshot residue provides a spectral signature that is readily apparent, but a person who has fired a single shot from a clean gun is not so easy to identify. The error rates associated with the LIBS identification of a subject who fired one shot from a clean gun have been evaluated by Monte Carlo simulation techniques, and criteria are proposed for defining a positive or a negative test result. © 2003 Optical Society of America

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1. Introduction

The detection of gunshot residue (GSR) particles on the hands of a suspected shooter has been an integral part of forensic science for the past 70 years. The Mexico City police department introduced the dermal nitrate test for the presence of GSR in 1933.[1] The method relied on the color development produced from the reaction of unburned particles of nitropropellant compounds but was flawed by numerous false positives. Matches, urine, fertilizers, fingernail polish, and some pharmaceuticals produced positive results. Harrison and Gilroy published the first test for the inorganic components of GSR in 1959.[2] Reagents were added in sequence to test for the presence of barium, lead, and antimony. The presence of these three elements remains the basis of modern forensic GSR analysis.

Insight into the formation of GSR is important in understanding how the presence of Ba, Pb, and Sb is indicative of a firearm discharge. An ammunition cartridge casing contains a small insert called a primer cap. The primer cap contains an initiator or primary explosive, an oxidant, and a fuel. During a firearm discharge, the firing pin strikes the primer cap and ignites the primary explosive. Then the oxidizer increases the temperature of the reaction until the fuel is ignited. Finally, this mixture ignites the propellant and forces the bullet down the barrel of the gun.

Nearly all primer caps contain lead styphnate initiator, barium nitrate oxidant, and antimony sulfide fuel.[3] Residual particles of Ba, Pb, and Sb vaporize in the high-temperature, high-pressure environment of a discharge. Openings in the gun allow these vapors to escape into the air, where they coalesce and form the particulate matter known as gunshot residue. Particles are distributed about the area of the discharge, including the hands and clothing of the shooter. Examination of the resultant residue has been divided into two categories, particle and bulk analysis.

Particle analysis techniques such as scanning-electron microscopy energy-dispersive spectroscopy[4] (SEM/EDS) use 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 a morphology consistent with GSR and contains Ba, Pb, and Sb, the particle is unambiguously identified as having originated from a cartridge discharge. Similar particles that contain only two of

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the three components are classified as characteristic of GSR.[1,3,5]

Bulk analysis involves the tape-lift or moist swab method of sampling. Techniques such as flame atomic absorption spectroscopy,[6] graphite furnace atomic absorption spectroscopy,[7] neutron activation analysis,[8] anodic stripping voltammetry,[9] and inductively coupled plasma atomic emission spectroscopy[10] have been used for the detection of Ba, Pb, and Sb on the hands of a suspected shooter. All these techniques rely on the generation of a hand-blank database to report the naturally occurring background level of the GSR metals. Once threshold values have been established, positive or negative results can be assigned by comparison to the library.

Careful use of the hand-blank library is crucial to the success of bulk analysis techniques. Several occupations have been identified in which workers are exposed to events that produce residues similar to GSR. Ideally, a suspect sample would be compared to a collection of blanks from the same occupational and behavioral background.[5,7] Examples of GSR-similar occupational samples exist in the literature for users of cartridge-operated industrial tools,[11] automobile brake mechanics,[12] and pyrotechnicians.[13] Fortunately, multielement techniques can be used to determine the presence of metals that did not originate from a firearm discharge. Research has shown that 99% of cartridge tool discharges, such as from high-power nail guns, also contain iron.[11] Pyrotechnics often contain potassium, aluminum, magnesium, or iron.[13]

The key to avoiding false-positive results in bulk analysis is the ability to monitor multielement emissions simultaneously. At present, inductively coupled plasma atomic emission spectroscopy and mass spectroscopy are the only bulk analysis methods available for the simultaneous monitoring of GSR metals. However, laser-induced breakdown spectroscopy (LIBS) should also be capable of rapid, sensitive, and simultaneous analysis of GSR.

Laser-induced breakdown refers to the process by which the focused energy of a laser beam exceeds the breakdown threshold value at the focal distance and forms a plasma.[14] When the energy from a laser is properly focused onto an analytical sample, the resultant plasma may be used for mass removal and as an excitation source in atomic emission spectroscopy. Atoms of analyte are raised to an excited state in the high-temperature plasma and emit characteristic radiation as they return to the ground state.

Surprisingly, no attempts have been made to identify GSR by use of LIBS. However, there have been several reports of the use of LIBS for detection of Ba, Pb, and Sb in matrices other than GSR. Eppler *et al.* determined concentrations of Ba and Pb in pressed sand and soil matrices.[15] LIBS has been used extensively for the identification of metal alloys, many of which contain GSR metals.[16] Recently LIBS was used for the analysis of metal ions (including Ba and Pb) bound to ion-exchange polymer membranes.[17] The application of LIBS to the detection of GSR is a logical extension. The multielement nature of LIBS should ensure a small number of false-positive results when from analyses for the detection of GSR. Elements that are not characteristic of GSR (such as those found in cartridge-based industrial tools and pyrotechnics) should be identified with ease. Additionally, LIBS offers the advantage of requiring no sample preparation. Tape-lift samples of GSR may be mounted directly into the LIBS instrument. The focused energy of the laser will couple with GSR metals without the addition of an electrically conductive surface (as is needed for scanning-electron microscopy).

Law enforcement agencies have expressed interest in determining whether LIBS can be used as a screening method to help to differentiate shooters and nonshooters at the scene of a crime. Inasmuch as LIBS can be made field portable and has the ability to identify the elements of which small particles are composed, it is a logical candidate for that purpose. We report in this paper the development of a LIBS technique for the field detection of GSR on the hands of a suspected shooter. We have generated a small library of spectra and have measured the error rates (the probabilities of generating false-positive and false-negative results) by Monte Carlo simulation of LIBS spectra near the limit of detection.

2. Experiment

A. Formation of Gunshot Residue

Gunshot residue was formed by firing rounds of Winchester 9-mm Luger 115-grain full metal jacket bullets (Winchester, East Alto, Illinois) through an Intrac HS 2000 handgun (HS Arms, Croatia), sold currently as the Springfield Armory Service Model XD 9101 (Springfield Armory, Geneseo, Illinois). Rounds were fired at an outdoor range by an experienced shooter who adhered to all range safety policies.

B. Sample Collection

Sample collection stubs were fabricated from commercially available materials. Strips of rod-shaped polypropylene [1-in. long by 0.5 in. in diameter (2.54 cm $\times$ 1.27 cm)] were cut on a lathe. 3M Scotch brand permanent double stick tape was pressed to the polypropylene stub, and 3M 5490 PTFE extruded film tape was pressed to the exposed side of the double stick tape. The 3M 5490 PTFE extruded film tape was chosen because of the low-emission background of the silicone-based adhesive and Teflon backing. All sampling stubs were sealed in 1-in. I.D. glass vials until they were needed for sample collection. A gloved technician handled all sampling stubs. 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 based on results of a comprehensive plume study performed by Schwoeble and Exline.[3]

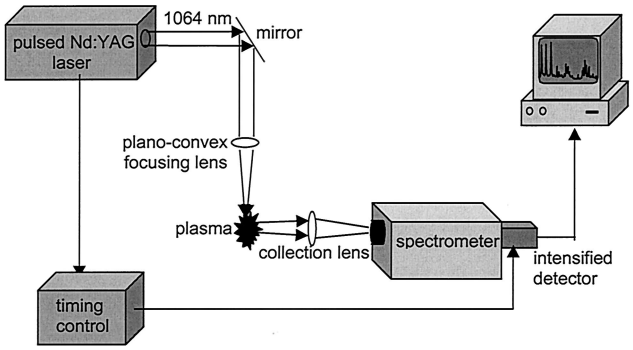

Fig. 1. Block diagram of the LIBS instrumentation.

C. Detection of Gunshot Residue

A Surelite I-10 Nd:YAG laser (Continuum, Santa Clara, California) operated at 1064 nm with 200-mJ pulses was used as the ablation source. The laser beam was focused by a plano–convex quartz lens with a focal length of 75 mm. The focal point was set 3.0 mm below the surface of the sample to minimize breakdown above the surface. Emission from the plasma was collected by a 25-mm plano–convex quartz lens with a focal length of 100 mm and was transferred into a fiber-optic cable. The fiber-optic cable transmitted the emission radiation to a Mechelle 7500 DiCam-PRO echelle spectrometer (Multichannel Instruments AB, Stockholm, Sweden). Camera control and spectral data collection were accomplished by a Dell OptiPlex GX1 computer running Multichannel Instruments software. Spectra were displayed by GRAMS/32 version 5.1 Spectroscopic Data Analysis Software (Galactic Industries Corporation, Salem, N.H.). A block diagram of the LIBS instrumentation is shown in Fig. 1, and individual components are specified in Table 1.

The emission signal from a LIBS plasma is time dependent, and most researchers use the time dependence to optimize signal-to-noise ratio. A delay of 3 μs was used to discriminate against the early-occurring continuum emission. The atomic emission spectra were integrated for 30 μs following the delay. These times were not optimized but represent general conditions used for most samples in our laboratory.

D. Monte Carlo Simulations

LIBS spectra were simulated with the aid of the random-number generator in Excel software (Microsoft, Redmond, Wash.). We used a spreadsheet function to add normally distributed random noise to spectral features to determine the error rates in the measurement of gunshot residue when the amounts were near the limit of detection.

3. Results and Discussion

A. Sample Homogeneity and the Use of Maximum Emission Data

A single laser shot vaporized the entire residue and most of the tape below; multiple shots provided no additional information and increased the background. All spectra consisted of the emission observed from one laser pulse. The 1-cm collection stub was sampled by the laser in 20 locations (a 4×5 grid spaced approximately 1.5 mm apart) to maximize the signal. Inasmuch as GSR occurs as individual particles distributed randomly about the sample collection stub, it is possible for only one of 20 laser shots to strike a GSR particle; thus averaging will decrease the signal-to-noise ratio. Instead of

Table 1. LIBS Instrumentation

Laser Component	Description
Laser System	
Laser	Continuum Surelite I-10 Nd:YAG laser (Continuum, Santa Clara, California)
Laser pulse	200 mJ, 7 ns
Rod diameter	6 mm
Beam divergence	0.6 mrad
Ablation spot	0.3-mm diameter
Irradiance	4×10^{10} W cm^{-2}
Mirrors	25-mm diameter, 45° high energy, 1064 nm, 99.9% reflecting (Newport, Irvine, California)
Optics	25 mm diameter, 75-mm focal-length plano–convex lens (Coherent, Auburn, California)
Powermeter	Model EPM1000 single-channel joulemeter–powermeter (Molectron Detector, Portland, Oregon)
Spectroscopic Component	
Optics	25 mm-diameter, 100-mm focal length plano–convex lens (Coherent, Auburn, California)
Detector	Mechelle 7500 DiCAM-PRO with echelle spectrophotometer and Mechelle software (Multichannel Instruments AB, Stockholm, Sweden)
Wavelength range	200–1000 nm
Delay time	3 μs
Gate time	30 μs
Data Analysis	
Computer	Dell OptiPlex GX1 (Dell Computers, Round Rock, Texas)
Software	GRAMS/32 version 5.1 spectroscopic data analysis software (Galactic Industries, Salem, N.H.) Microsoft Excel 97 (Microsoft, Redmond, Washington)

averaged or summed spectra, we record the maximum emission observed. The maximum spectrum is the largest observed signal at each wavelength in any of the 20 individual spectra obtained from the sample. The spectra discussed hereafter all refer to maxima, unless otherwise noted.

B. Hand-Blank Library

A library of blank spectra was generated from samples obtained from the hands of 20 volunteers. Volunteers were allowed to participate only if they had not fired a gun within 24 h before sampling.

C. Test Firings

Seven large emission lines were observed in the LIBS spectra of GSR; all were later identified as Ba lines. Next, LIBS spectra from the hands of a shooter who fired a single shot were obtained. The experiment was repeated to produce a total of six replicates. Contact with a gun that had previously been fired was found to transfer detectable amounts of gunshot residues, so the gun was scrupulously cleaned before each firing. We analyzed the LIBS spectra (maxima of 20 laser shots) to determine the magnitude of the signal that corresponds to a single gunshot. LIBS emission spectra representative of both a blank and a positive test for GSR are presented in Fig. 2. Each of these spectra represents an individual laser pulse, not composite spectra formed from the maximum signals at each wavelength.

D. Statistical Analysis

First we evaluated the background by analyzing the hand-blank library spectra to determine the mean and the standard deviation of the blank, σ, at each of the seven analytical wavelengths. Next, the spectrum from the hand of the suspect was compared to the blank at each wavelength. If the signal from the suspect exceeded that of the blank at a specified confidence limit, then the test was considered positive for GSR. This process was repeated for each of the 7 principal emission lines in the GSR spectrum and for all 6 shooters, for a maximum of 42 possible positive tests. The number of times that the sample exceeded the blank by 3σ (or a 99% confidence interval) was noted and is presented in Table 2. The table shows that the 3σ limit was exceeded 12 times by the shooter who fired a single shot and 40 times by the shooter who fired 5 shots.

E. Determining the Error Rate

If the method is to be used as evidence in Federal court, its error rates must be known.[18] Because the LIBS method can be used either to eliminate nonshooters or to identify shooters, both error rates must be considered. An error of the first kind is a false negative, in which a person has fired a gun and the test results indicate that he or she has not fired a gun. An error of the second kind is a false positive, in which a person has not fired a gun and the test results indicate that he or she has fired a gun.

The confidence level based on results at multiple wavelengths cannot be calculated analytically. A Monte Carlo mathematical simulation determined the error rates for tests at the seven analytical wavelengths. One thousand blank spectra were generated; the mean and the standard deviation of the blank library were used. We created spectra that emulate gunshot residue near the limit of detection

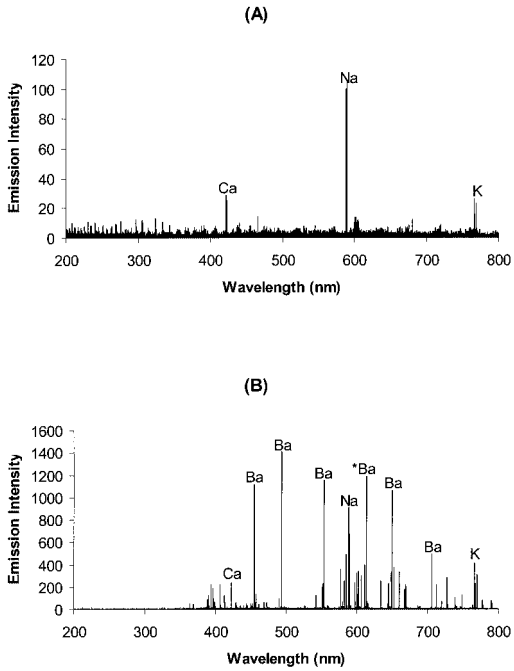

Fig. 2. Representative laser-induced breakdown spectra. Instrumentation and parameters are described in Table 1. (A) Representative emission spectrum of a blank. Sampling stub applied to the hand of a nonshooter. Predominant emission lines are attributed to Ca (I) 422.6728, Na (I) 588.9950, Na (I) 589.5924, K (I) 766.4911, and K (I) 769.8974. (B) Representative emission spectrum of a positive GSR test. Sampling stub applied to the hands of a person who has fired five shots from a clean gun. Emission lines indicative of GSR are Ba (II) 455.403, Ba (II) 493.409, Ba (I) 553.548, Ba (II) 614.172, *doublet Ba (II) 649.690, Ba (I) 649.876, and Ba (I) 705.994.

Table 2. Results of Test Firing Experiments

Experiment	Replicate	Number of Wavelengths at Which the Signal Exceeds the Blank by 3σ
Single shot fired from a clean weapon	1	2
	2	1
	3	1
	4	1
	5	1
	6	6
Five shots fired from a clean weapon	1	7
	2	7
	3	7
	4	7
	5	7
	6	5

Table 3. Number of Wavelengths at Which the Sample Exceeds the Blank Based on 1000 Simulated Spectra

Number of Wavelengths That Tested Positive	Sample Exceeds Blank by 1.5σ		Sample Exceeds Blank by 3σ	
	Did Not Fire Gun	Fired Gun	Did Not Fire Gun	Fired Gun
0	16	0	117	0
1	73	0	276	1
2	216	0	309	6
3	276	1	197	32
4	256	8	81	70
5	125	58	19	194
6	36	154	1	372
7	2	779	0	325

by adding to the blank the increase in signal caused by a single gunshot. We analyzed the simulations numerically to determine the number of instances in which a single gunshot provided enough signal to exceed a threshold value at each of the seven analytical wavelengths. In addition, the number of times that the blank exceeded the threshold because of random noise was determined. Two thresholds were used, one based on the signal's exceeding the blank by 1.5σ and the other by 3σ, where σ represents the standard deviation of the blank at a particular wavelength.

The results obtained from the simulation in which a positive result is assigned to a signal that exceeded the blank by 1.5σ are shown in Table 3 and illustrated in Fig. 3(A). Of 1000 suspects who did not fire a gun, 16 tested negative at all wavelengths (zero positive results), 73 had only one positive test, etc. Of 1000 individuals who fired a single shot from a clean gun, 779 tested positive at all seven wavelengths, 154 tested positive at 6 wavelengths, etc. The data can be used to set a standard with a known error rate. One possible standard might be that a suspect has to exceed the blank by 1.5σ at four or more wavelengths before the field screening test result is considered positive. Following this criterion, 99.9% of all people who have fired a gun will be so identified correctly and 41.9% of people who did not fire a gun will be detained for further analysis. The 1.5σ test minimizes false negatives.

There are situations in which minimizing false positives might be a goal, for example, to prevent incarcerating an innocent person. A 3σ threshold [Fig. 3(B)] and a criterion of exceeding the threshold at 6 or 7 wavelengths can be used. Only 1 person of 1000 who had not fired a gun would be detained by these criteria; however, 30.3% of those who did fire a gun would be freed. The 3σ threshold minimizes false-positive results and may be used in screening by application of two different decision levels. A person who tests positive at zero wavelength can be confidently identified as a nonshooter, a person who tests positive at seven wavelengths can be confidently identified as a shooter, and anyone who tests in the intermediate range can be recommended for additional testing.

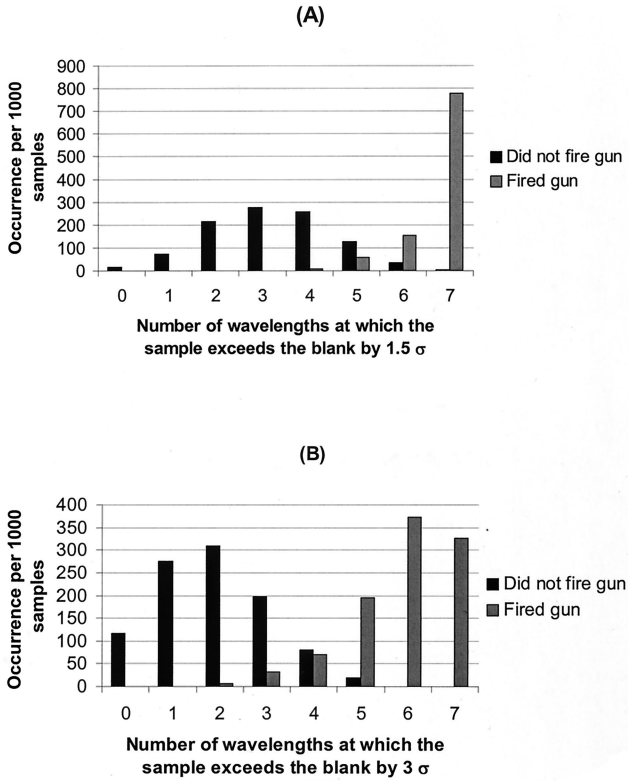

Fig. 3. Predicting error rates by mathematical simulation. The number of wavelengths at which 1000 samples, each sample representing the GSR from firing a single shot from a clean gun, exceeds the background by a specified amount. (A) The sample exceeds the blank by at least 1.5σ. (B) The sample exceeds the blank by at least 3σ.

The choice of a criterion (1.5σ or 3σ) is important in determining the error rate, but one could improve the rate by optimizing the LIBS parameters, by sampling at more than 20 locations on the sampling stub, and by reducing the spectral background.

4. Conclusions

Although the LIBS method of detecting gunshot residue has not been fully optimized, its potential for use as a screening method is clear. The use of the maximum signal, rather than the average, allows LIBS to detect the presence of particulate matter, such as GSR, on the hands of a suspected shooter. Error rates can be established by simulation, and criteria developed to minimize false-positive and false-negative identifications.

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