# DEVELOPMENT OF A LASER-INDUCED BREAKDOWN SPECTROMETER FOR LEAD-FREE GUNSHOT RESIDUE ANALYSIS

by
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ABSTRACT
RYAN ALEXANDER GREGG: Development of a Laser-Induced Breakdown Spectrometer for Lead-Free Gunshot Residue Analysis
(Under the direction of Dr. Nathan Hammer)

Research has demonstrated that Laser-Induced Breakdown Spectroscopy (LIBS) can be used as an effective method of screening for the common elemental components in gunshot residue. Barium (Ba), lead (Pb), and antimony (Sb) make up the primer cap of most ammunition involved in forensic gunshot residue analysis. Recently, ammunition manufacturers have started producing and popularizing ammunition with zinc (Zn), titanium (Ti), and gadolinium (Gd) primer components that are non-toxic to the environment. This paper discusses the development of the Ole Miss Department of Chemistry and Biochemistry's first LIBS instrument for forensic analysis of lead-free using Gd as a tracer element for identification purposes. A Silva method of sampling was adopted using a non-emissive 3M tape to lift GSR from the subject's hands after firing the weapon. Samples using the lead-based and lead-free bullets were analyzed by LIBS system consisting of an Ocean Optics USB2000 CCD Camera with a Continuum 1064 nm Nd:YAG laser as the excitation source. Each sample was analyzed by multiple laser pulses fired at various locations on the sample surface. Spectra was taken from Ba, Pb, Zn, and Gd standards and emission lines were identified for all elements but Gd. Lead-free and lead-based gunshot residue sample spectra were also obtained, but were found to be too noisy for emission line identification due to the lack of a time-controlled camera system. Further discussion in this thesis describes how this problem can be rectified so that this project may continue in the future.

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# 1 Overview of Gunshot Residue

Gunshot residue (GSR) is the term given to the group of small particles released from the discharge of a firearm. These particles can be collected by forensic scientists and analyzed to provide useful evidentiary data in solving crimes. This chapter is an introduction into the composition and mechanism of GSR particle formation. This overview will be concluded by a discussion of the methods of GSR analysis, as well as the forensic application of GSR data.

## 1.1 Mechanism of Formation and Composition

The mechanism behind the formation of GSR comes directly from the chemical reactions that take place when a firearm is discharged. On the back of all ammunition cartridges is a small circular container that holds all the necessary chemical components for the bullet to fire. This container, known as the primer cap[1], holds the three different types of chemicals that work in conjunction to expel the bullet from the cartridge. The three chemicals found in the primer cap are the initiator, fuel, and the oxidant.

The firearm discharge begins when the pulled trigger causes the firing pin to strike the outside of the primer cap, causing the initiator to ignite[1]. As the initiator continues to burn, the oxidizer will provide the oxygen necessary to increase the heat of the reaction to a temperature where the fuel can be ignited. The heat from the reaction of the primer mixture will escape the cap and enter into the chamber containing the propellant (also known as gunpowder) through two entrance points called flash holes[2]. Due to the increase in heat, the propellant begins to

change from the solid phase to the gas phase, consequently causing a buildup in the pressure behind the bullet. As the pressure continues to build up in the chamber, the bullet will be expelled from the cartridge towards the end of the barrel. While the bullet is being propelled out the end of the barrel with the propellant, the gas mixture of the propellant and the primer components (known together as the GSR plume) can exit the weapon through the end of the barrel or other firearm openings. Such openings could include the moving slide of a handgun or the swing out cylinder of a revolver. Upon being expelled from the firearm, the GSR plume will expand outward and eventually land onto a surface, causing the gas particles to rapidly cool. The common surfaces utilized for the collection of GSR in forensic analysis will be discussed in later sections.

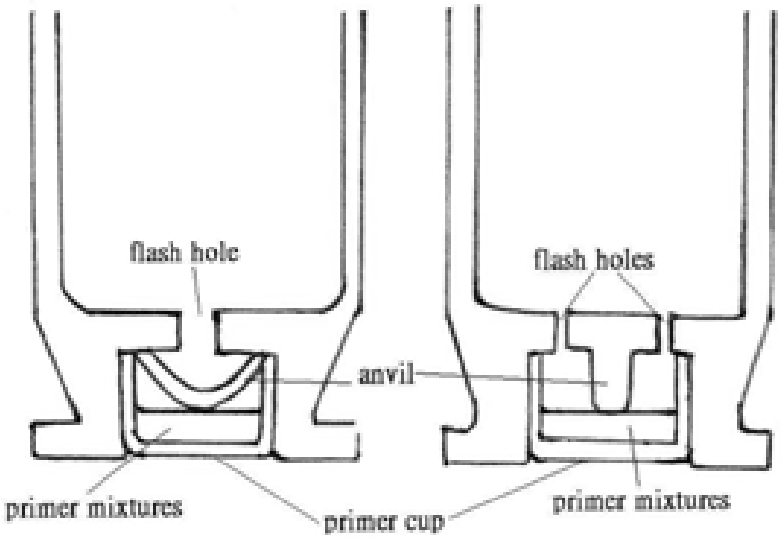


**Fig. 1.1- Comparing Boxer (left) and Berdan (right) primers**

Figure taken from Hsien-Hui Meng, H.-C. L. Forensic Science Journal 2007, 6,39.

Each different type of bullet will have different compartmental structures inside the primer cap. Centre-fire primer cap structures, which accounts for the majority of all firearm

ammunition, can be divided into the three main classes; Boxer, Berden and Battery Cup[2]. Boxer and Berden primer caps are primarily used in smaller arms, such as pistols or revolvers, while Battery Cup's are almost exclusively used in shotguns. The main difference between the Boxer and Berden caps is the location of the anvil, a small structure between the primer cap and the propellant. When the firing pin strikes down on the primer cap after the trigger is pulled, the anvil serves the purpose of being the surface that the crushed primer components strike and ignite. Boxer and Berden primer caps have different anvil shapes, causing the structure of the flash holes to be different between these two types. Fig 1.1 above illustrates these two different structures. The Boxer anvil is in a half circle shape and therefore leaves room for only one flash hole with a larger diameter. The Berden anvil is in a T-shape and is characterized by two smaller flash holes located on each side of the anvil. Boxer primers are the more popular primers in the United States, while the Berden primers are popular in other countries.

The composition of the primer mixtures in ammunitions have evolved into many new groups of primer classifications over the past century. Modern day ammunition primers are divided into three classes; mercuric, non-corrosive and lead-free primers[2]. Mercuric primers are found in older military ammunition and have become less popular during the past half century. The composition of these primers includes mercury fulminate as the initiator, potassium chlorate as the oxidizer, and lead azide as the fuel. The reason behind the lack of popularity in these mercuric primers is that the primer is composed of corrosive elements that can decrease the lifetime of the barrels in firearms. The potassium chlorate would form potassium chloride during the combustion reaction and consequently cause the gun to hold in moisture that deteriorates the inside of the barrel. The mercury present also caused deterioration of the guns barrel by amalgating with the brass case of the bullet. The discovery of mercuric primer corrosion lead to the formulation of non-corrosive primers using entirely new primer

components. The non-corrosive primers consist of a lead styphnate initiator, barium nitrate oxidizer, and antimony sulfide fuel. The reliability and consistency of this combination of primer components has made non-corrosive primers the overwhelming favorite among all ammunition manufacturers while continuing to be the most researched class of primer component.

The last class of primers, lead-free primers, has become more popular in recent years as ammunitions manufacturers have become more environmentally conscious. This class of primers has chosen to replace the toxic Ba, Pb, and Sb compounds with less hazardous compounds like Al, Si, Cu, Zn, Ti, S, and Ca[6]. Lead-free primers have also become popular among indoor gun rages due to the removal of hazardous gases from the enclosed space of indoor facilities. This thesis will focus primarily on analyzing lead-free primer ammunition, specifically the SINTOX® Ammunition from RUAG Holding Inc. The primer components of those bullets consist of zinc oxide and titanium dioxide, with a gadolinium tracer compounds. All of these components have a significantly Threshold Limit Value than those of the non-corrosive primers and are considered environmentally safe[7]. Chapter 3 will discuss the analysis of the SINTOX® Ammunition in greater detail.

## 1.2 Methods of Gunshot Residue Analysis

The specific testing options that have been developed to identify gunshot have changed dramatically over the past several decades. These tests include basic colorimetric tests, tests by instrumental bulk analysis, and tests by instrumental particle analysis. Colorimetric tests have been developed for the analysis of the different components of GSR since the early 1930's. The first of the colorimetric tests used for GSR was the melted paraffin test, which involved taking melted wax and allowing it to harden on a suspect's hands[3]. After the wax had hardened, it was removed from the hands and mixed with a solution of N,N-diphenylbenzidine[4] that identified

the nitroglycerine or nitrocellulose present in gunpowder by turning them blue. A modern day version of the nitrate tests using diphenylamine is still in use today[3].

Colorimetric tests focusing on the particles of GSR are still in use today both as presumptive and field test methods. Harrrison and Gilroy first developed the two test method of identifying the barium, lead and antimony particles in GSR in 1959[4]. The first test involved two reagents that were coupled together to systematically identify antimony and lead. Triphenylmethylarsonium was first added to produce a complex with antimony that produced an orange color. Following the presence or absence of an orange color, sodium rhodizonate was added to produce a red color if barium or lead was present. A diluted solution of hydrochloric acid was added in last to serve as a confirmation of the presence of lead by forming a deep purple color. Since 1959, many forensic laboratories have shortened this colorimetric test to only use the sodium rhodizonate and hydrochloric acid test. This test was found to have significantly fewer false positives than the paraffin test and can be performed in a much smaller period of time.

The purpose of colorimetric tests has changed significantly since the shift of forensic scientists towards instrumental techniques. While colorimetric tests don't have the same significance in conclusively identifying GSR in criminal investigations, they now serve the purpose of contributing to probable cause that can justify further investigation into certain suspects. These tests have also been converted into portable field tests and are in use by many law enforcement agencies around the country. The ability to test for GSR at a crime scene decreases the possibility of the suspect losing GSR due to washing or contact with other surfaces and consequently helps investigators get more accurate data to conclude that further testing is necessary. The inexpensive nature of these field tests for GSR also means that forensic

laboratories will save money on more expensive instrumental tests by eliminating suspects negative for GSR by preliminary colorimetric tests.

Bulk analysis of GSR consists of analyzing the entire concentration of the elemental components that make up GSR instead of the individual particles. For GSR analysis, numerous bulk analytical techniques have been evaluated for their efficiency at identifying GSR in a sample. The primary bulk analysis methods researched for GSR detection today are atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and laser-induced breakdown spectrometry (LIBS)[5]. Other less popular methods that have also been investigated include neutron activation, anodic stripping voltammetry, and X-ray microfluorescence.

Atomic absorption spectrometry is one of the oldest analytical methods used in determining qualitative and quantitative information about the elements that make up a bulk sample. This analytical method focuses on the elemental components of a mixture converting into the gas phase and absorbing characteristic wavelengths of radiation. This radiation consequently raises those element's electrons to an excited energy level. The result of this analysis is a spectrum of absorption lines for each individual element. AAS has been used in forensic laboratories to identify the Ba, Pb, and Sb primer components collected from a suspect. Forensic laboratories use different sampling methods used to collect the GSR (lift tape, swabs, etc.) and as a result, forensic laboratory instrumentation can include a number of different atomizers to convert the solid sample into the gas phase for analysis. Examples of atomizers used for GSR analysis range from routine flame AAS to electrothermal atomizers such as carbon rods, tantalum strip, and graphite furnace systems[4].

Benefits that come from utilizing AAS for GSR analysis include its ability to analyze multiple elements simultaneously and its low cost to purchase and operate. While AAS may have these advantages, it also has many serious disadvantages for applications in forensic science. The detection limits for AAS limit its application to samples taken only from the most concentrated areas where GSR is found[4]. Even in such concentrated areas as the shooting hand, AAS has too high of detection limits to quantify Sb and Ba in samples. The results of AAS analysis have also been found to have inconsistent concentration data. This inconsistent data is especially troubling in forensic analysis, as the results from these analyses are under heavy scrutiny by both crime labs and the court system.

ICP-MS is a powerful analytical tool that has been applied to the analysis of GSR in the past two decades. Like AAS, ICP-MS gives elemental quantitative and qualitative information about a sample. The difference between ICP-MS and AAS is that while AAS is an optical method, ICP-MS uses the theory of mass spectrometry to create a spectrum based on the mass-to-charge ratios of the elements found in the sample. This occurs by first preparing a sample into an acidic solution that can be analyzed by the ICP-MS[6]. A nebulizer will convert the solution into an aerosol form and send the analyte into the torch chamber containing "inductively coupled" argon gas. The "coupling" occurs as the argon gas is exposed to energy given off by an RF coil and high energy plasma is formed to atomize the sample. The atoms exit the torch and enter into the mass spectrometer where they are separated and analyzed based on their mass-to-charge ratios.

The overall design of an ICP-MS makes it very useful in analyzing trace and ultratrace concentrations, like those found in GSR samples. ICP-MS has lower detection limits than AAS and has the ability to have automatic sample introduction, thus decreasing the amount of time

spent by a forensic analyst in programming the instrument. The sample preparations done in ICP-MS are also very effective in reducing the interferences from the sampling matrix. Lastly, ICP-MS has the ability to do isotope ratio studies of GSR samples, which can indicate the abundance of specific isotopes of Pb, Sb, and Ba found in a given sample[7]. The decrease in detection limit does produce some issues that impact the efficiency of ICP-MS in forensic analysis. The sample preparation required to get the sample into a solution that can be made into an aerosol is time consuming. For certain samples, long periods of heating in an oven or other techniques like microwave digestion may be required to purify the sample for the ICP-MS[6]. This is problematic for forensic labs that see a large number of samples per day, especially due to the importance of producing results for a large number of samples. Cost is also an issue for many government labs with tight budgets, as ICP-MS instruments can cost two to three times as much as an AAS instrument.

Particle analysis is a far more definite method of identifying specific groups of elements in particle form instead of analyzing the collection of a certain elements in the sample as whole. Particle analysis with GSR is considered the most sensitive and accurate of analytical techniques in identifying the components of GSR. GSR particle analysis is performed exclusively using scanning electron microscopy (SEM), an analytical technique that focuses a concentrated beam of electrons onto a sample surface to produce X-ray emission spectra[8]. The incident beam of electrons interacts with the elements in the sample to knock out the inner orbital electrons, leaving a void in the electron orbital. Electrons from higher orbitals will begin to cascade downward to fill the void and will simultaneously release X-rays in the process. Like other methods of optical spectroscopy, each X-ray wavelength given off from the sample is unique to a particular element. In addition to the X-ray spectrum collected from the sample, the beam of electrons from the SEM produces a magnified image of the sample that far surpasses any image

created by a standard optical microscope. SEM has the ability to magnify an image up to 100,000X to the point where detailed images of microscopic particles of GSR can be characterized and identified based on their morphology. While having emission spectra for identification of individual elements is helpful, it is the ability to study particle morphology that makes SEM so effective. Researchers have found GSR particles to take one of three morphological classes; uniform 1-10 μm spheroids, irregular shaped particles formed as a result of heated fusion of smaller particles, and layered particles with a Pb outside with Sb and Ba making up the core[5].

SEM is considered the most effective method of analyzing GSR due to its ability to produce a wide array of useful and specific data. Identifying a sample particle of GSR based on both emission spectra and morphology gives an even greater assurance of accuracy during testing. Other benefits include low detection limits, the ability to automate SEMs to computer controlled scanning, and non-destructive testing of samples[9]. These benefits do come with disadvantages that are especially troublesome for forensic laboratories. The sensitivity of an SEM instrument can often lead to analysis of several different particles found on a sample that aren't GSR. Some of these compounds can include other environmental elements or biological contaminants from sampling[4]. This can add extra work for analysts to have to rule out particles that aren't of interest and that work can slow down a forensic scientist who has a large caseload. Cost is a very important issue in using SEM as well. SEM instruments equipped with the necessary detectors and scanning capabilities for forensic analysis of GSR can cost into the hundreds of thousands of dollars, not including the necessary costs for the sample preparations and maintenance. The factor of the cost makes it such that only certain crime labs can afford these instruments, while others are forced to use alternative means of analysis.

## 1.3 Forensic Applications

The obvious application of identifying GSR on a suspect is to determine whether or not a person in question for a crime has recently discharged a firearm. This information is vital in violent gun crimes such as homicides, assaults, and suicides. The process of collecting the evidence for these types of crimes can be very challenging. One of the most difficult tasks for any forensic scientist or crime scene investigator is being able to successfully identify any aspect of a crime scene as containing possible evidence. This can be especially complicated when dealing with such microscopic particles like GSR. The mechanism of the formation and dispersion of GSR after the firing of a gun has been studied to determine where the most likely places that GSR can be found and identified by analysis. The most common places to find GSR are located on the hands, face, clothes, and various other objects in the environment of the firearm discharge.

Deposition of GSR on the hands is most commonly due to the hands being in close proximity to the firearm openings that the GSR plume exits after the firearm is discharged. It is for this reason that the hands contain the highest concentration of GSR particles as well and why GSR sampling methods for testing suspects heavily relies on sampling the hands. The most common areas for sampling on the hands are the back side and inside palm of each of the hands[5]. Many forensic researchers have also targeted more specific areas of the hands. Dockery and Goode used the first knuckle of the trigger finger, webbing between the thumb and trigger finger, and the first knuckle of the thumb in their analysis of GSR on the hands of a shooter[10]. Research done by several different scientists has determined the hands to be the most likely place for GSR deposition and will be the area of sampling done in Chapter 3.

When using the hands as the location for sampling, several different factors may cause the accelerated loss of GSR particles from the hands. Some of these factors include the type of firearm and ammunition used, the age and condition of the weapon used, the personal hygiene habits of the shooter, and various different environmental factors[9]. For example, two studies have been conducted to specifically analyze the lifetime of gunshot residue on a shooters hands using Laser Induced Breakdown Spectroscopy (LIBS). Rosenberg and Dockery first discovered that signal averaging of GSR spectra using LIBS produced an exponential decay function where the intensity of the signal could be tracked until there it was impossible to distinguish from the background[1]. The result from this study was that GSR can be successfully found using LIBS for up to 5.27 days after discharging a firearm, even when the person sampled undergoes their normal activities. Silva and Cortez later confirmed this study by successfully identifying characteristic peaks for Ba and Pb in samples taken from subjects who had fired one or two rounds from a pistol, washed their hands, and been sampled 16 hours later[9].

When searching a potential suspect for GSR, the face, clothing and crime scene environment normally serve as secondary locations for testing. For larger firearms like rifles and shotguns, the face can have deposition of GSR from the shooter looking down the sight[5]. Clothing can be a great alternative option for testing when a suspect has washed their hands after firing a weapon. The small particle size of GSR can penetrate into the textile material in clothes and be sampled using the same tape-lift method employed for all other sample surfaces. The environment surrounding a firearm discharge can also be important to see who or what has come into contact with GSR particles. Based on the Locard Exchange Principle, two objects that come into contact with each other will have an exchange of material[5]. This principle is the basis behind trace evidence examination at crime scenes and also applies to trace GSR evidence.

Examples of this principle can be seen in instances where a suspect can transfer GSR after a firearm discharge to any surface they touch, including clothing, vehicles, walls, or other people.

Identifying the pattern of GSR particles at the point of contact for the bullet provides another important forensic application of determining shooting distance. Researchers have determined that there is a correlation between the distance from a shooter to the point of impact and the concentration and distribution of the GSR found at impact. Discharging a firearm closer to the bullet's point of impact will have a great concentration of GSR present due to the limited distance necessary for the GSR particles to travel. The same principle applies for bullets fired at a long distance from the impact points having a lower concentration of GSR. As the distance from the firearm to discharge increases, there will also be a significant increase in the size of the area where GSR will deposit. This phenomena is due to the GSR plume expanding out of the barrel in the x,y, and z plane directions. Identifying the pattern of GSR dispersion after firearm discharge can be done using many of the colormetric tests discussed earlier in this chapter.

When forensic evidence is presented in court, the analyst who was responsible for interpreting the evidence will act as an expert witness by testifying to their experimental findings. One of the most important parts of testifying in court as an expert witness is providing an explanation of the experimental data in a manner simple enough for the jury to comprehend. This is especially true in identifying unknown trace elements such as GSR. To do this, forensic scientists created a classification system to simplify results of trace GSR particle analysis to simplistic adjectives describing the evidence. The first design of this classification system was done by Wooten et al[4] in 1979 in his study of GSR from handguns. Wooten's study is considered the most extensive study to date involving SEM application for classifying GSR evidence, and

because SEM is still the best way of analyzing and classifying GSR evidence, many of Wooten's ideas from his research are still in use.

When GSR is analyzed, the detection of certain elements in the primer will place the data in a certain classification. Classifying evidence as "unique to GSR" requires the detection of a Pb-Ba-Sb, Ba-Sb, Pb-Ba-Ca-Si-Sn, or Ba-Ca-Si-S particle in the sample[4]. Other particles containing only some of the particles in the "unique to GSR" classification are placed in the "consistent with GSR" group. Such particles include Pb-Sb, Sb (although very rare), Pb-Ba, Pb, and Ba if S is not present. This classification group describes particles that are less likely to originate solely from a GSR origin.

GSR is not the only possible source of producing the particles found in the "consistent with GSR" category and consequently false positives can result. The most common source of false positives occurs in the relatively common use of Ba and Pb in a number of different manufacturing and automotive jobs. Mechanics are commonly exposed to barium and lead when dealing with car batteries, tires, and brake components[9]. Many construction workers and warehouse workers that interact with cartridge-based tools like nail guns and staple guns will commonly test positive for GSR due to the similar construction of the primers in these tools with those with bullets. After identifying the possibility for false positives in testing, many forensic labs have began to reevaluate the words they are using to describe GSR evidence. "Characteristic with GSR" has come to replace "unique to GSR" in many crime labs due many scientists believing that "unique with GSR" had too many implications of certainty in the results.

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# 2 Laser Induced Breakdown Spectroscopy

Atomic emission spectroscopy has become the cornerstone of analytical chemistry by contributing methods of identification and quantification of unknown elements present in samples. Many different analytical methods have been developed in this subspecialty of analytical chemistry including Laser Induced Breakdown Spectroscopy. This instrumentation uses pulses from a laser to excite samples into a plasma form and subsequently measure their emitted radiation. This technique has a wide variety of applications and is at the forefront of many different areas of optical spectrometry research. The following will describe the theory and instrumentation of LIBS, as well as this instrument's advantages, disadvantages, and applications in chemistry.

## 2.1 Theory and Instrumental Design

The theory behind LIBS came from the discovery of the fact that optical radiation can cause a dielectric breakdown in molecules and elements[1]. This discovery came in 1960, but it wasn't until 1963 that Debras-Guédon and Liodec[2] first used LIBS for studying different types of surface materials. The source of the optical radiation used to exceed the breakdown threshold in this method is laser light, thus giving LIBS its name. While LIBS has applications for all states of matter, the theory behind LIBS differs slightly between these different states. Gas particles can be directly sampled after exposure to the laser light, while solid and liquid samples work by

ablation. Ablation is a process by which a small portion of a solid or liquid material is removed from the bulk of the solid or liquid by converting it into the gas or plasma phase through vaporization. In LIBS, ablation produces a plume of vaporized materials that have very low concentrations ranging from micrograms to nanograms. Because solids are the most popular state of matter for samples undergoing LIBS analysis, this is the theory behind the majority of LIBS sampling.

The formation of the plasma by laser light excitation is the most important theoretical part of the LIBS instrumentation. First, a short duration pulse of radiation from the laser source hits the surface material. The energy from the laser pulse causes a phenomenon known as "avalanche ionization"[1] where the free electrons that are excited from the exposure to the laser pulse are accelerated by the electric fields associated with the pulse in the period between collisions. Those free ions contribute to a high level of optical absorption by the sample. Ions form as the free electrons collect due to the laser pulse, and the consequent build up in free electrons continues acceleration, creating the "avalanche" effect. This effect also contributes to the high amount of heat associated with the plasma, which can reach temperatures up to 10,000 K before reaching thermodynamic equilibrium[3]. Once this process reaches the minimum irradiance (power per unit area) needed to convert to plasma from whatever state of matter the sample was previously in, the breakdown threshold will be exceeded and plasma will be formed[1].

Plasma exhibits similar physical properties of gases, and as such will begin to expand outward as the size of the plasma increases. The expansion of the plasma, however, is conducted at supersonic speeds in the form of an expanding shock wave[2]. As the plasma plume expands towards surrounding gas molecules, the velocity of expansion decrease over time as

the plasma collides with the air molecules. The plasma propagation will continue as the sample is still being exposed to the source light, causing continued absorption of radiation by the plasma and excitation. The excitation of the sample into the plasma state causes the individual elements to occupy higher energy states than the original ground state. Each element of the Periodic Table has discrete energy levels that electrons will occupy after being excited. Decay from these higher energy states is primarily accomplished through emission of electromagnetic radiation, with each of discrete energy levels corresponding to the emission of a unique wavelength of light. It is these unique wavelengths of light emitted from each element that makes it possible for LIBS to (theoretically) detect the presence of every element on the Periodic Table. Figure 2.1 illustrates a database used in physical chemistry to detail the emission wavelength and emission intensity of different elements. This figure shows the emission wavelengths of Gd, one of the elements discussed in Chapter 3.

**Relative intensity of gadolinium lines observed in an arc of copper containing 0.1 atomic percent of gadolinium**

*Strong lines of gadolinium*

| Intensity | Wavelength A | Spectrum | Energy levels K | Term combination |
|---|---|---|---|---|
| 850 | 3768. 39 | II | 633–27162 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{4\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{10}F_{4\frac{1}{2}}$ |
| 700 | 3422. 47 | II | 1935–31146 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{5\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{10}F_{7\frac{1}{2}}$ |
| 600 | 3646. 19 | II | 1935–29353 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{5\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{10}F_{6\frac{1}{2}}$ |
| 550 | 3350. 47 | II | 1159–30997 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{3\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{10}D_{6\frac{1}{2}}$ |
| 550 | 3362. 23 | II | 633–30367 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{4\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{8}D_{5\frac{1}{2}}$ |
| 550 | 3584. 96 | II | 1159–29045 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{3\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{10}D_{4\frac{1}{2}}$ |
| 500 | 3796. 37 | II | 262–26595 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{3\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{10}F_{3\frac{1}{2}}$ |
| 500 | 3850. 97 | II | 0–25960 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{2\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{10}F_{1\frac{1}{2}}$ |
| 440 | 3358. 62 | II | 262–30027 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{3\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{8}D_{4\frac{1}{2}}$ |
| 440 | 3545. 80 | II | 1159–29353 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{3\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{10}F_{5\frac{1}{2}}$ |
| 440 | 3743. 47 | II | 1159–27865 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{3\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{10}F_{5\frac{1}{2}}$ |
| 440 | 4225. 85 | I | 1719–25376 | $4f^7 6s^2 5d^1\ a\ {}^{9}D_{3}^{\circ} — 4f^7 6s^1 5d^1 6p^1\ y\ {}^{9}F_{3}^{\circ}$ |
| 420 | 3852. 45 | II | 262–26212 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{3\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{10}F_{3\frac{1}{2}}$ |
| 400 | 3549. 36 | II | 1935–30101 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{3\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{10}D_{3\frac{1}{2}}$ |
| 380 | 3654. 62 | II | 633–27988 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{4\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{8}P_{3\frac{1}{2}}$ |
| 360 | 3813. 97 | II | 0–26212 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{2\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{10}F_{2\frac{1}{2}}$ |
| 320 | 3850. 69 | II | 633–26595 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{4\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{10}F_{3\frac{1}{2}}$ |
| 300 | 3100. 50 | II | 1935–34179 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{3\frac{1}{2}} — 4f^7 5d^1 6p^1\ y\ {}^{10}P_{2\frac{1}{2}}$ |
| 300 | 3656. 15 | II | 1159–28502 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{3\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{10}P_{2\frac{1}{2}}$ |
| 300 | 3687. 74 | II | 2857–29966 | $4f^7 6s\ 5d^1\ a\ {}^{8}D_{1\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{8}D_{2\frac{1}{2}}$ |
| 280 | 3439. 99 | II | 1935–30997 | $4f^7 6s\ 5d^1\ a\ {}^{10}D_{3\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{10}D_{6\frac{1}{2}}$ |
| 280 | 3463. 98 | II | 3444–32304 | $4f^7 6s^2\ a\ {}^{8}S_{3\frac{1}{2}} — 4f^7 5d^1 6p^1\ y\ {}^{8}P_{4\frac{1}{2}}$ |
| 280 | 3783. 05 | I | 999–27425 | $4f^7 6s^2 5d^1\ a\ {}^{9}D_{3}^{\circ} — 4f^7 6s^1 5d^1 6p^1\ x\ {}^{9}P_{4}$ |
| 260 | 3664. 60 | II | | |
| 260 | 3712. 70 | II | 3082–30009 | $4f^7 6s^1 5d^1\ a\ {}^{8}D_{3\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{8}D_{3\frac{1}{2}}$ |
| 260 | 4078. 70 | I | 533–25044 | $4f^7 6s^2 5d^1\ a\ {}^{9}D_{4}^{\circ} — 4f^7 6s^1 5d^1 6p^1\ y\ {}^{9}D_{5}$ |
| 240 | 4053. 64 | I | 999–25661 | $4f^7 6s^2 5d^1\ a\ {}^{9}D_{3}^{\circ} — 4f^7 6s^1 5d^1 6p^1\ y\ {}^{9}D_{6}$ |
| 240 | 4058. 22 | I | 215–24850 | $4f^7 6s^2 5d^1\ a\ {}^{9}D_{3}^{\circ} — 4f^7 6s^1 5d\ 6p^1\ y\ {}^{9}D_{4}$ |
| 240 | 4098. 61 | II | 6605–30997 | $4f^7 5d^2\ a\ {}^{10}F_{7\frac{1}{2}} — 4f^7 5d^1 6p^1\ z\ {}^{10}D_{6\frac{1}{2}}$ |
| 240d | 4325. 57 | II | 11067–34179 | $4f^7 5d^2\ a\ {}^{10}P_{4\frac{1}{2}} — 4f^7 5d\ 6p^1\ y\ {}^{10}P_{4\frac{1}{2}}$ |
| | 4325. 69 | I | 533–23644 | $4f^7 6s^2 5d^1\ a\ {}^{9}D_{4}^{\circ} — 4f^7 6s^1 5d^1 6p^1\ y\ {}^{9}F_{4}$ |

**Fig. 2.1 Table from database of Gd emission lines**

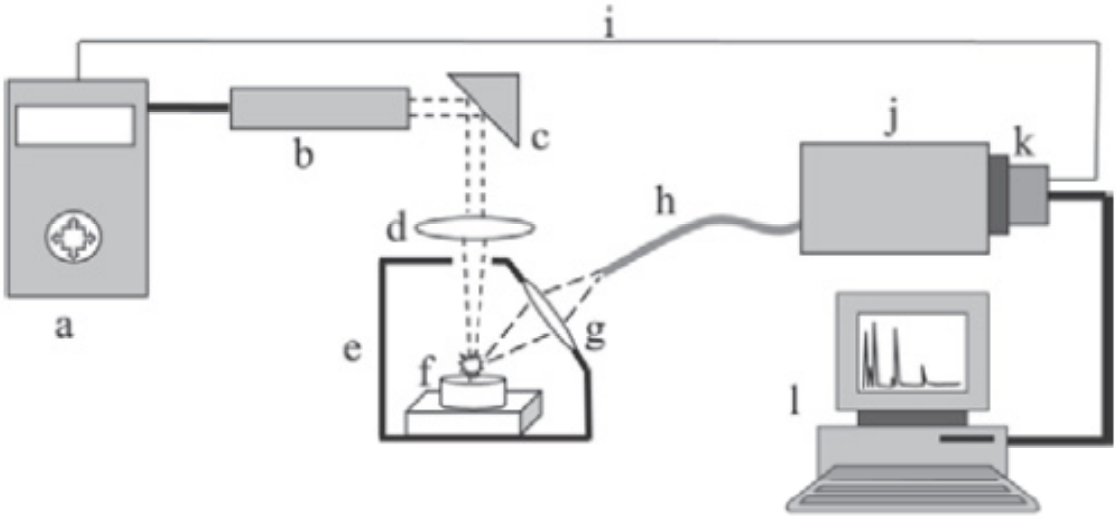
**Taken from Standards, N. B. o. Tables of Spectral-Line Intensities Arranged by Elements; Commerce, U. S. D. o., Ed., 1975**

The cooling and relaxation of these excited species can also occur by a number of different processes, including collisions with other gas molecules, quenching, recombination of ions and free electrons, heat, and radiation[4].

A couple of important optical phenomena are associated with the LIBS method that directly impact the way the instrument is set up and the spectra is produced. The first phenomenon is plasma shielding, a phenomenon impacting the amount of the laser pulse the sample is exposed to. As stated previously, the plasma plume will propagate simultaneously as the laser pulse continues to hit the rest of the sample. The result of this is that the laser light will be absorbed by the plume of excited atoms, ions, and free electrons and will not reach the core of the sample to cause further ablation[2]. Another source of plasma shielding includes surrounding gas elements absorbing the light themselves, such as in argon and helium vacuum systems. Plasma shielding can result in minimizing the concentration of the analyte that is ablated into the plasma phase, consequently limiting the amount of analytically significant radiation emitted.

The second phenomenon is the Stark effect, a phenomenon that occurs due to the presence of the free electron field formed after exposure to the laser pulse. Collisions with the high density free electron field in the plasma causes emission of radiation near the same resonant wavelength as the emission that is analytically useful[1].

**Fig. 2.2 Schematic Diagram of a LIBS System**




(a)Laser source and cooler; (b) pulsed laser head; (c) mirror; (d) focusing lens; (e) excitation chamber; (f) sample; (g) collecting optics; (h) optical fiber; (i) detector trigger signal; (j) wavelength selector; (k) detector array and (l) microcomputer

Figure taken from Pasquini, C.; Cortez, J.; Silva, L. M. C.; Gonzaga, F. B. Journal of the Brazilian chemical Society 2007, 18, 463.

The result is a peak broadening effect that is primarily found in the beginning nanoseconds of exposure to the pulse, specifically the time of the initial ablation of the sample material. This continuum radiation not associated with an analytically useful signal, called the Bremsstrahlung emission or “white noise”, will diminish over the small amount of time it takes for the free electron density to shrink. The effects of Bremsstrahlung radiation on the experimental data will be discussed in detail in Chapter 3.

The LIBS instrumentation, show in Figure 2.2[3], has a very simple design that makes it a stationary or portable instrument. The laser excitation source can vary depending on the particular analyte or method in question, but the majority of LIBS experiments utilize the neodymium-doped yttrium aluminum garnet (Nd:YAG) laser. This laser has natural harmonics used at 1064 nm and 532 nm. The majority of the applications for LIBS have used 1064 nm, as it

offers the highest power density, higher possible plasma temperatures, and increase absorption[1]. Using the higher 1064 nm harmonic of the Nd:YAG laser also benefits the experimental design in that 1064 nm is out of range of most detectors used in LIBS. Using 532 nm lasers opens up the possibility for the detector to collect laser light reflected from the source, thus interfering with possible emission wavelengths around 532 nm. Q-switched lasers are most often used due to their ability to produce a pulsed beam with very high output power. Some more expensive setups for LIBS will also include a second laser, with the hope that the double laser source LIBS will be able to maintain the plasma by exciting the plasma region again[3].

A focusing lens is used to take the collimated laser light and focus it on a very small point on the samples surface. For solid samples, this focused point is the point of ablation. Sample chambers can be in high vacuum, although it is not necessary in all cases. At a 45 degree angle to the incident light, there is another lens that will focus the emitted radiation onto a fiber optic cable that will collect the light. While this lens may help optimize the experimental design by collecting more of the emitted light from the sample, it is not the only method of collecting light from the sample. The experimental method used in Chapter 3 involves collecting light with the fiber optic without a lens, so that the optic can be placed in an optimal position for each different location on the sample surface.

The collected light travels through the fiber optic until it reaches the wavelength selector. Spectrophotometers are then used to disperse the emitted radiation on the focal plane for analysis by the CCD camera detector. Due to the fact that there are very small wavelength differences between the emitted radiation of the many different elements possibly in the analyte, having a high resolution spectrophotometer is very important for this method. A prism

and grating combination (echelle monochromator) is typically used to get this type of resolution in LIBS. CCD cameras are the typically used detector due to their high resolution and two dimensional structure, but alternative one and two dimensional setups with photomultiplier tubes and photodiode arrays have also been used as well[2]. Most LIBS detectors are optimized by using a combination of electronic components that ensure spectra are only taken when analytically significant emissions are present. These components include a pulse generator, a controlled shutter located in front of the detector, and trigger for the detector to take spectra. When all three of these parts work together in unison, the detector is safe from potentially harmful "white noise" radiation and clear spectra can be seen after the Bremsstrahlung radiation has subsided. The importance "gated" detectors will be discussed in more detail in Chapter 3.

A spectrum from LIBS is displayed by computer software as a graph of wavelength of emission on the x-axis and intensity (with counts as an arbitrary unit) on the y-axis. As previously stated, the optimum method for obtaining good spectra with easily distinguishable analyte emission peaks is to gate the detector to start integrating after the electron density goes down, which is normally around 10-1000 ns[3]. Interpretation of the spectra involves identifying the most abundant peaks on the spectrum by their wavelength. Databases like the US Army LIBS Elemental Database can be used to identify experimental spectrum peaks to those found in previous literature to help identify the element's specific emission wavelength and ionization state[4].

## 2.2 LIBS Advantages and Disadvantages

There are a great number of advantages in using LIBS as a method for atomic emission spectroscopy. The first, and arguably most important, is that LIBS requires no sample

preparation. Unlike methods such as ICP-OES, ICP-MS or graphite furnace atomic absorption spectrometry, LIBS requires no purification of the sample. This fact makes LIBS a great method for non-soluble analytes that still can be ablated or gas particles that are difficult to manipulate. The lack of sample preparation also makes LIBS a very speedy method for elemental analysis[1]. When dealing with many bulk samples, such as samples found in environmental or forensic labs, being able to turn out a high rate of sample analysis during a day is essential and LIBS has an optimal design for achieving that goal.

Another convenient aspect of LIBS is that there is little to no sample destruction by this method. The use of a focusing lens to ablate the material usually only causes craters to form in the sample at less than 20 microns per pulse[3]. Having minimal sample destruction opens up the possibility for multiple analyses on the same sample, even in samples of low concentration. In addition, using a focusing lens can make it such that spatial distribution of the craters can open up possibilities for analysis of spatial influences on concentrations, as well as doing depth profiles by firing laser pulses all in one spot. The last advantage of LIBS is that small amount of simple components allows for LIBS to be both inexpensive and portable. With portability in the instrument comes the possibility of in situ analysis[2] and rapid elemental analysis in the field.

Disadvantages of using LIBS stem primarily from the advantage of not having any sample preparation. Sample preparation serves the purpose of creating a purified and homogenized sample for analysis. The ablation process of LIBS doesn't account for inhomogeneous samples and thus can hurt the significance of the analytical results found from this method. This problem with homogeneity is exacerbated by the fact that LIBS is a point detection method[1] and problems with the bulk sample non-uniformity can contribute to poor figures of merit. Precision is directly determined from the homogeneity of the sample and thus precision is found to be

smaller than many other analytical methods in LIBS. To counteract this problem with precision, many LIBS methods will use multiple points of sampling along the sample surface to determine whether or not the analyte is present.

The higher detection limits of different elements using LIBS can also be a disadvantage. LIBS is a bulk analysis method that analyzes the total element concentration of a specific point on the sample. The area of ablation in LIBS is small and thus the plasma plume contains a small amount of the analyte emitting low amounts of light. Higher concentrations are necessary at the specific point of sampling to produce adequate emission for detection of specific wavelengths corresponding to specific elements. These higher concentrations limit LIBS analysis to trace elements and reduce the possibility of ultratrace analysis.

Surface contamination on solid samples can also cause problems in LIBS due to the ablation not forming plasma of the true elemental composition of your analyte. Since all elements will emit light when excited, contamination of the sample that has a concentration around that of the analyte can falsely indicate that other elements are present in the sample. Instruments that don't have very high resolution can also show peak broadening when emission from contaminant elements emit around the same wavelength as analyte emission.

The last major concern with LIBS is the safety concerns[2]. LIBS instrumentation, as previously stated, primarily uses the 1064 nm fundamental wavelength as the laser excitation source. While this wavelength provides better spectra, the fact that it is in the non-visible IR region of light makes it dangerous to work with. Special care is also taken to build sample structures that prevent source laser light from reflecting or refracting from the sample chamber to anywhere close to the analyst. Working at the high power output that LIBS requires with IR

source radiation can bring a level of danger to the user and should be considered whenever samples are analyzed.

## 2.3 Experimental Applications

LIBS has been used for elemental analysis in many different kinds of matrices over the past couple decades. The primary focus of LIBS research and literature has centered on the detection of certain metals in a number of different matrices. This focus is due to LIBS being an elemental detection method and not a molecular detection method. The overwhelming majority of the matrices where LIBS analysis has been done on metals are specifically focused on the environment and the detection of toxic metals in various parts of the environment. Research applicable to this thesis has also been conducted in analyzing GSR with LIBS.

Having no sample preparation makes environmental testing perfect for LIBS instrumentation because it allows researchers to analyze samples both in the field and in the lab. Examples of the numerous types of environmental testing include Gondal et al. analyzing contaminants found in lipstick[5], Siddiqui et al. analyzing trace metals from organic wastes[6], Godoi et al. analyzing the metals found in the production of children's toys[7], and Li et al. evaulating experimental parameters on the analysis of elements in coal[5,8] . These four examples were selected from the hundreds of publications involving LIBS and elemental analysis from environmental matrices. One of the best examples of the application of LIBS in the field has been numerous scientists doing feasibility studies of using LIBS for elemental analysis on the Mars rover. Sirven's publication in 2007 describes a study done in a lab to simulate whether or not using LIBS to identify elements in the soil on Mars is possible[9].

Three major publications have discussed the use of LIBS for GSR analysis. The first publication was written by Dockery et al. in October of 2003[10]. In this paper, Dockery outlines the application of LIBS for the detection of GSR on the hands of the shooter. Dockery is also the first author to detail the sampling procedure by which all publications pertaining to LIBS and GSR have adopted. This procedure involved using 3M 5490 PFTE extruded film tape on a polypropylene plastic base. The experimental parameters of Dockery's study, specifically related to the irradiance, delay time and data collection time, were also an important base from which the other authors would later use. The results of Dockery's experiment were that seven possible Ba peaks from a standard Winchester 9mm Luger bullet were clearly distinguishable from those of a hand blank, indicating a positive test for GSR. Monte Carlo simulations were also conducted to show that majority of the positive spectra had more than three wavelengths identified that exceeded the blank by 3σ. Dockery's conclusion was that the method wasn't optimized completely at the time, but that the simulations proved that the error rates could be improved with more research.

Rosenberg et al. authored the second publication on GSR detection with LIBS, but focused on GSR lifetime studies with LIBS instead of GSR identification[11]. His publication used the same sampling method as Dockery's, but used Ba (II) emission at 455.403 to establish the signal detection limit and the intensity of the signal to constitute a positive test. This information was used to continually test subjects who had discharged a firearm over time until their spectra had the Ba(II) emission below the signal detection limit. Several samples were run and the overall results of the experiment concluded that GSR could test positive on a shooter's hands 5.27 days after the discharge of the firearm.

The most recent publication on using LIBS for GSR detection was authored by Silva et al. in 2009[12]. This publication took Dockery's work and optimized many different aspects of the experimental setup and discussed the effect of samples being exposed to different situations. Silva used a sampling method of firing 20 shots in a rectangular pattern on the sample surface and collecting the best spectra from each. He also took spectra from different people who had fired a gun and washed their hands, people worked around machinery or occupations that are known to cause false positives and hadn't fired a gun, and people who had not fired a gun in 48 hours. The results of these tests were that people who had fired a gun and washed their guns still tested positive and that the false positive theory was confirmed. Positive results were identified by emission peaks from Ba and Pb. This setup for using LIBS as a screening for the presence of GSR is the optimal setup in literature today.

Although these three authors have made tremendous strides in applying LIBS to the detection of GSR, a void still remains in the literature. All of the authors have done their studies on bullets that have lead-based primers. While this type of ammunition is currently the most popular, the environmentally friendly lead-free primers are beginning to grow more popular. While literature is currently available that looks at lead-free primers with SEM, no publications currently exist applying LIBS to identifying GSR from lead-free primer ammunition. As these environmentally friendly lead-free primers begin to grow more popular, they will eventually be involved in criminal activity that will need to be analyzed by forensic scientist. It is necessary to ascertain whether or not it is possible to determine the presence or absence of GSR from these lead-free primers using LIBS before LIBS can be adopted as a consistent GSR screening method in crime labs.

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# 3 Analysis of Lead-free GSR Using LIBS

At the end of Chapter 2, the void in GSR detection research using LIBS was identified for those types of ammunition that are classified as “lead-free” or “environmentally-friendly.” This chapter will discuss the construction of the Ole Miss Department of Chemistry and Biochemistry’s first LIBS apparatus, the experimental components and parameters used, and the results and conclusion from the data obtained throughout the experiment.

## 3.1 Introduction

This thesis has three primary objectives:

1. To develop the Ole Miss Department of Chemistry and Biochemistry’s first LIBS instrument.
2. To obtain standard and sample spectra of GSR from both lead-based and lead-free primer components.
3. To identify whether or not emission lines from Gd in lead-free RUAG SINTOX® primers could serve as an elemental tracer specific to this type of ammunition.

Literature currently exists applying other analytical methods to the detection of lead-free GSR, including SEM-EDX[1] and X-ray microfluorescence[2], but LIBS research has never been published on this specific lead-free GSR application. Successful identification of the elements found in lead-free primers would make LIBS a more viable option for crime labs to use this instrument as a screening method for GSR.

Of all the types of lead-free primer ammunition currently available, this thesis specifically analyzed the RUAG Copper Matrix NTF SINTOX® Lead-free 9mm Luger Frangible round (See Fig. 3.1).

**Fig. 3.1 Picture of Lead-free primer bullet box sitting on top of Nd:YAG laser**

This specific round was chosen due to the unique components that make up the primer. The SINTOX® primer is composed of Zn, Ti, and Gd oxides. RUAG, the Swiss company that produces this ammunition type, advertises Gd as a tracer substance that is put into their ammunition for the detection of GSR[3]. This ammunition is already being used by both German and Dutch Police[4], as well as the German Army[3].

Using Gd as a tracer substance is particularly useful because it is a lanthanide rare-earth metal that doesn't provide as many opportunities for false positives in testing due to its rarity. LIBS spectra of Gd has also already been published before and several emission lines have been identified from the different ionization forms of Gd (See Fig 2.1)[5]. Ti and Zn also have had

publications detailing the specific emission lines characteristic of those elements using LIBS[6]. Because each element has been successfully identified by LIBS emission lines in other matrices, all of these elements put together in a GSR-matrix sample should be identifiable by LIBS. This theory is the base of the third goal of this thesis.

## 3.2 Experimental

*LIBS Components*

The LIBS apparatus used in this thesis was built from a combination of materials already found in the Hammer Physical Chemistry Group in the Department of Chemistry and Biochemistry. The excitation source used was a Continuum Surelite Nd: YAG laser operating at 1064 nm at 1.36 kV with a 250 μs Q-switch delay. Each pulse of the laser was fired manually using a single shot cable. The cage built to hold the sample consisted of a ThorLabs IR 100 mm. focusing lens mounted on a movable slide to control the position of the focusing lens in both the X and Z plane directions. The sample box was closed during sampling to prevent contamination from the outside room lights and to ensure the safety of the analyst from the IR laser light.

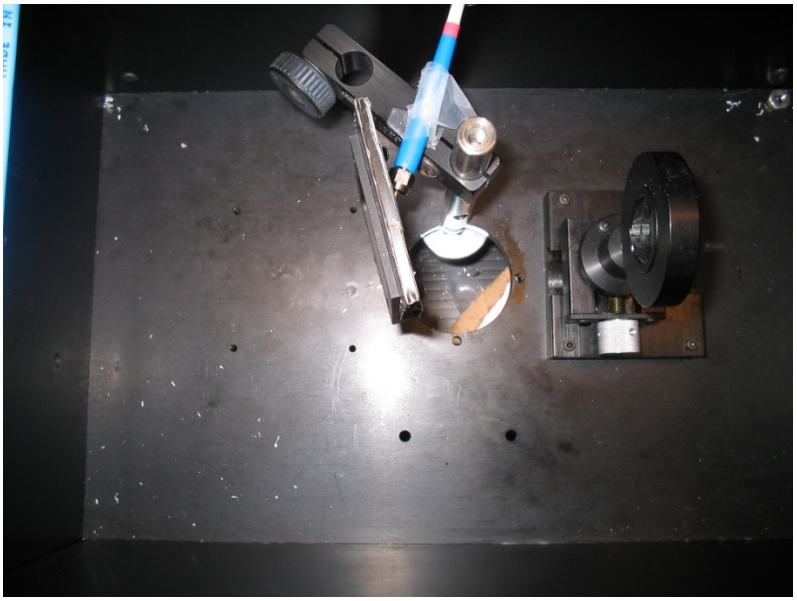

**Fig. 3.2 Top view of the cage setup including the focusing lens, sample surface and optic cable.**

The sample surface was held upright by an optic stand with two clamps (Fig. 3.2). A fiber optic cable was placed at a 90° angle to the sample, with the collecting end of the optic being

positioned less than a millimeter away from the sample surface. The collecting end of the optic was placed so closely to the sample to ensure maximum collection of the emitted light. The fiber optic focused the light into an Ocean Optics USB2000 Miniature Fiber Optic Spectrometer (2048 pixel CCD camera) running OOIBase32™ Spectrometer Operating Software with an integration time of 300 msec.

*Sampling Procedure and Standards Used*

A tape-lift method was used to collect all samples during this experiment. The sample surface was constructed using a piece of black plastic cut to fit the clamps on the optic stand. The plastic was covered on the sampling side first with Scotch® double sided tape, then with 3M 5490 PFTE extruded film tape. The 3M tape was chosen as the outer tape to sample with due to its low emission background[7].

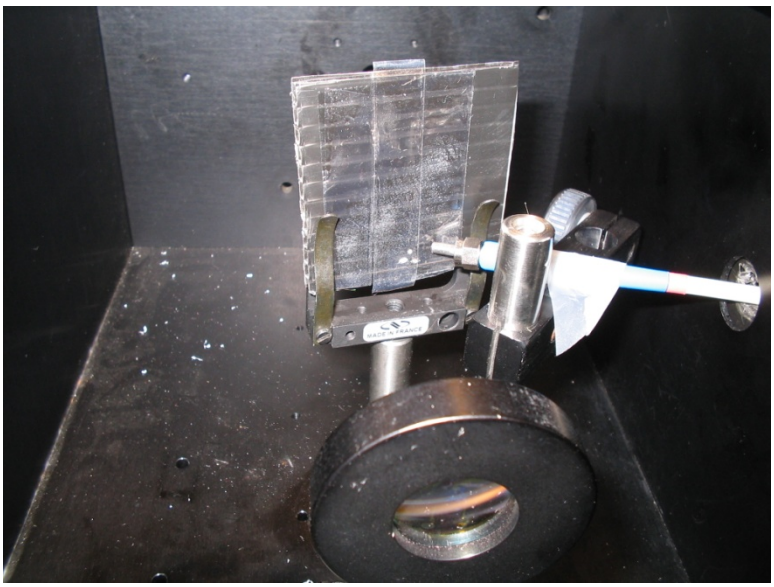

**Fig. 3.3 view from the front side of the sample surface inside the cage**

All test fires occurred outdoors at Sardis Lake under optimal weather and safety conditions. The first test subject fired six shots with a Heckler and Koch USP Compact .40 Smith and Wesson pistol using Winchester .40 Caliber Reloaded pistol rounds. The second test subject fired six shots with a Beretta Model 92 9mm pistol using the RUAG Ammotec SINTOX® Primer Copper-Matrix NTF 9mm Luger Frangible pistol rounds. A hand blank was also taken from a person who hadn't fired a gun in over a week. Different handguns and ammunition were used with the lead-free and lead-based ammunition to avoid cross contamination with the samples.

The caliber change between the weapons played no part in altering the deposition of the GSR. Each gun had been thoroughly cleaned before use and each test subject had not discharged a firearm in the week before sampling to avoid contamination.

After the subjects fired their pistols, a sample was taken by a gloved analyst by pressing the adhesive tape surface on the skin of the hands. The locations of sampling, including the first knuckle of the first finger, the webbing between the first finger and thumb, and first knuckle of the thumb, were those described as the highest areas for GSR deposition by Schwoeble and Exline[8]. Each location had multiple contacts with the tape and the sample was immediately put into a clean beaker and sealed with Parafilm after sampling. Each sample was placed on the sample holder and twenty pulses from the laser were fired on the sample surface and the spectrum from those twenty pulses was analyzed.

Standard spectra was also taken for several of the elemental components of the GSR samples, including a Ba (FischerScientific Standard), Pb (FischerScientific Standard), Zn (FischerScientific Standard), and Gd (SigmaAldrich Standard) spectrum. The Zn and Pb standards were in a strip form that made it possible to mount it directly on the sample holder, while the Gd and Ba crystalline structures required the standards to be placed on the same type of adhesive surface as the GSR samples. Twenty laser pulses were also taken of each of the standards and the spectra from each standard was analyzed.

## 3.3 Results and Discussion

Fig. 3.4 shows representative spectra from each of the standards and samples. Each of these standards and samples was analyzed and the emission lines that were both

distinguishable from the noise and matching the emission lines from previous literature were labeled with their emission wavelengths and ionization states.

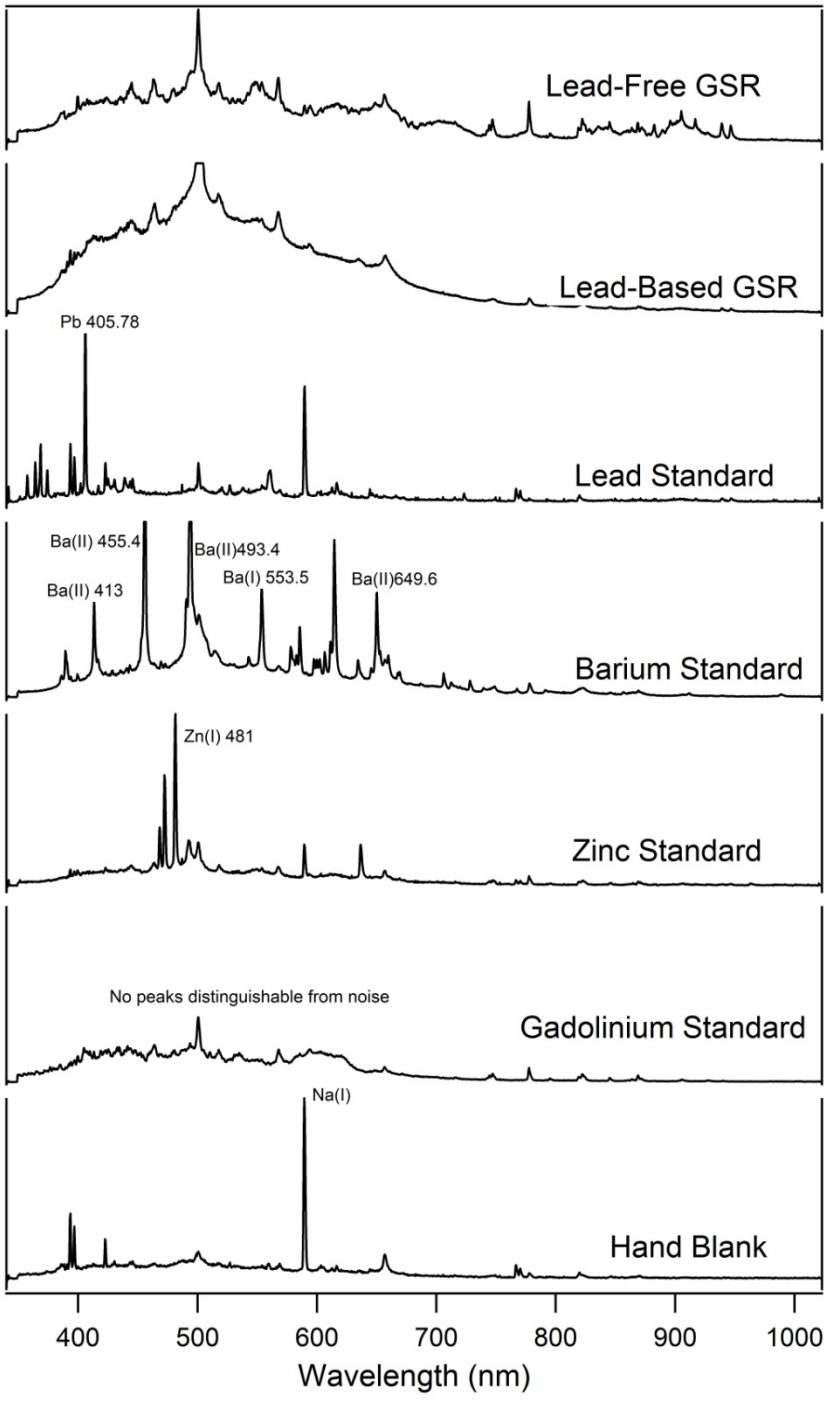


**Fig. 3.4 Spectra taken from each standard and sample with labeled emission lines**

There is a clear difference in the signal-to-noise ratio of the spectra taken from the standards and the samples. For all the standards (except Gd) the primary emission lines can be identified very clearly. The hand blank showed a strong peak of Na at Na(I) 588 nm. This peak was also found in hand blanks of other literature[7,9]. For the lead-based GSR elemental component standards, emission lines identified that correspond with emission lines from previous LIBS literature include the Ba standard at Ba(II) 413 nm, Ba(II) 455.4 nm, Ba(II) 493.4 nm, Ba(I) 553.5 nm, Ba(II) 649.6 nm, and the Pb standard at Pb 405.78 nm. For the lead-free GSR elemental component standards, the only emission line corresponding with emission lines from previous LIBS literature was in the Zn standard at Zn(I) 481. A Ti standard was not analyzed due to the lack of availability of the standard.

The standard for Gd had no emission lines that corresponded to any literature or database emission lines. The lack of emission lines in this standard spectrum can be explained when consideration is taken into what the literature emission peaks for Gd are and what equipment was used in the LIBS apparatus. Gd has several different emission lines located at Gd (I): 453.781 nm, Gd (II): 288.133 nm, 302.760 nm, 335.047 nm, 335.862 nm, 336.223 nm, 339.512 nm, 341.695 nm, 341.873 nm, 342.247nm , 343.299 nm, 346.899 nm, and Gd (III): 249.953 nm, and 297.542 nm[5]. The Ocean Optics CCD detector used in the LIBS instrument is limited to only acquiring signal from light emitted in the visible and IR range, meaning that all UV emission would not show up on the spectrum. With the exception of Gd (I) 453.781 nm, all of these characteristic emission lines for Gd are in the UV region and are thus out of the range of the detector (>350 nm). The one exception of Gd (I) 453.781 nm showed no emission peak on the spectrum that could be identified from the background noise. This Gd standard has shown that it isn't possible to identify Gd emission peaks with the current LIBS instrument detector due

to the overwhelming majority of the emission peaks having wavelengths outside the range of the detector and the peak in the range of the detector having a low intensity.

Both the lead-based and lead-free GSR samples showed a strong background continuum emission that greatly diminished the quality of the spectra overall. Because the continuum was so intense, no emission lines for the primer components can be identified with a high degree of confidence. The source of this continuum emission is the Bremsstrahlung radiation associated with the initial ablation of the sample material and formation of the plasma. As stated in Chapter 2, Bremsstrahlung radiation is formed by collisions with the high density free electron field in the plasma causes emission of radiation near the same resonant wavelength as the emission that is analytically useful. In the lead-free and lead-based sample spectra, this radiation results in the high intensity noise that makes identification of any specific elemental emission line impossible. This Bremsstrahlung radiation is exacerbated in the samples more than the standards due to the high density of the electron field of multiple elements instead of a single element, causing the continuum emission to be much higher the sample spectra than the standard spectra[10]. The background continuum also caused the detector to not be able to acquire emission immediately after the continuum emission due to the detector having to recover from saturation.

The issue of the continuum emission from the Bremsstrahlung radiation was addressed in the LIBS literature by using a detector that has the ability to control the time of data acquisition with very high precision. Because the continuum emission is generated at the moment of ablation and the start of the plasma formation, a delay before data acquisition can ensure that the brief lifetime of the Bremsstrahlung radiation is avoided all together. Silva and Dockery utilized a delay time of 3 μs with an data collection (integration) time of 30 μs and were

able to acquire emission spectra without any continuum radiation interference[7,9]. Using these parameters with the detector used in this thesis is not possible because the time control function of the Ocean Optics Spectrometer can only delay data collection in millisecond units, not microseconds. Delaying the data collection in milliseconds would miss the analytically useful emission lines all together, while not delaying the data collection causes saturation of the detector by continuum radiation and the formation of a spectrum that has no analytically significant emission lines. This problem with the lack of time-sensitive data acquisition demonstrates that the detector used in this thesis didn't have the ability to take adequate spectra and needs to be replaced.

## 3.4 Conclusions

This thesis outlined three overall goals: building Ole Miss Chemistry's first LIBS instrument, obtaining useful spectra of lead-based and lead-free GSR samples, and determining whether Gd can be used as a forensic tracer in GSR analysis. The construction of the LIBS instrument from the available components was an overall success. The spectra from the standards exhibited emission lines that matched those found in previous LIBS literature, however, the continuum background in the GSR sample spectra made it impossible to identify emission lines from elements making up the primer residues. Gd was determined to not be useful as a forensic tracer element in this thesis' LIBS setup due to the majority of Gd emission lines occurring in the UV region. To accomplish these goals in the future of this project, it will be necessary to replace the current detector with a detector that can do timed data acquisition in the microsecond range, as well as analyze sample light emission in the UV and IR regions.

## 3.5 References


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