

12-15-2012

A Comparative Study of Laser Induced Breakdown Spectroscopy and Spark Induced Breakdown Spectroscopy for Rapid Analysis of Mercury in Soils

Pavan Kumar Srungaram

Follow this and additional works at: <https://scholarsjunction.msstate.edu/td>

Recommended Citation

Srungaram, Pavan Kumar, "A Comparative Study of Laser Induced Breakdown Spectroscopy and Spark Induced Breakdown Spectroscopy for Rapid Analysis of Mercury in Soils" (2012). *Theses and Dissertations*. 57.

<https://scholarsjunction.msstate.edu/td/57>

This Graduate Thesis - Open Access is brought to you for free and open access by the Theses and Dissertations at Scholars Junction. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of Scholars Junction. For more information, please contact scholcomm@msstate.libanswers.com.

A comparative study of laser induced breakdown spectroscopy and spark induced
breakdown spectroscopy for rapid analysis of mercury in soils

By

Pavan Kumar Srungaram

A Thesis
Submitted to the Faculty of
Mississippi State University
in Partial Fulfillment of the Requirements
for the Degree of Master of Science
in Physics
in the Department of Physics and Astronomy

Mississippi State, Mississippi

December 2012

A comparative study of laser induced breakdown spectroscopy and spark induced
breakdown spectroscopy for rapid analysis of mercury in soils

By

Pavan Kumar Srungaram

Approved:

David L. Monts
Professor and Graduate Coordinator of
Physics and Astronomy
(Major Professor)

Jagdish P. Singh
Emeritus Research Professor of Physics
and Astronomy
(Director of Thesis)

Henk F. Arnoldus
Professor of Physics and Astronomy
(Committee Member)

Matthew J. Berg
Assistant Professor of Physics
and Astronomy
(Committee Member)

R. Gregory Dunaway
Professor and Interim Dean
College of Arts & Sciences

Name: Pavan Kumar Srungaram

Date of Degree: December 15, 2012

Institution: Mississippi State University

Major Field: Physics

Major Professor: Dr. David L. Monts

Director of Thesis: Dr. Jagdish P. Singh

Title of Study: A comparative study of laser induced breakdown spectroscopy and spark induced breakdown spectroscopy for rapid analysis of mercury in soils

Pages in Study: 45

Candidate for Degree of Master of Science

Elevated concentrations of mercury in soils are quite hazardous to flora and fauna and water bodies near these soils. This makes continuous monitoring of mercury very essential. This work compares two potential spectroscopic methods LIBS and SIBS at their optimum experimental conditions for mercury monitoring. The experimental conditions for Hg measurements with LIBS and SIBS were determined and calibration was developed. The limits of detection (LODs) of Hg in soil were calculated from the Hg calibration curves. The LOD for mercury (Hg) in soil calculated using LIBS and SIBS are 483 parts-per-million and 20 parts-per-million, respectively. The present study indicates that SIBS is more efficient with powder samples in a low concentration region for quantification of mercury in soils while LIBS is efficient in the region of higher concentrations using pellet samples. Both these techniques can be further investigated and improved for in-situ analysis of soils.

ACKNOWLEDGEMENTS

I am heartily thankful to my research advisor, Prof. Jagdish P. Singh whose guidance and support from the initial to the final level enabled to develop an understanding of the subject. His astute guidance has helped me to overcome the problems during my research, without which this thesis might not have been possible.

I express my sincere thanks to Ms Fang-Yu, Yueh Research Scientist-I, Institute for Clean Energy Technology, Mississippi State University, for her guidance and valuable suggestions which proved very helpful for my study. I would also like express to sincere thanks to Prof. David L. Monts, my major professor, for all the support he extended during my study. I take this opportunity to thank Dr. Henk F. Arnoldus and Dr. Matthew J. Berg who accepted to be in my graduate committee. I am grateful to Institute for Clean Energy Technology for providing excellent lab facilities to carry out my research work.

I am extremely grateful to the Department of Physics and Astronomy, for providing excellent classroom facilities, and for providing a very conducive atmosphere to carry out academic work. I also would like to thank the office staff; Ms Susan Galloway and Ms Connie Vaughn, for their cooperation.

I take this opportunity to thank my colleagues Krishna Kanth Ayyalasomayajula, Vivek Dikshit, Markandey M. Tripathi, Tracy Miller, and Charles Ghany for all their

support and for the fruitful discussions that happened during both course work and research.

I would like to express my thanks to my friend Sandeep and Tejaswi for their support.

I express my love, gratitude, and respect for my parents, who have always supported me in all my endeavors.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	ii
LIST OF TABLES	vi
LIST OF FIGURES	vii
CHAPTER	
I. INTRODUCTION	1
1.1 General Introduction	1
1.2 Theoretical Background.....	4
II. EXPERIMENTAL.....	8
2.1 Sample Preparation	8
2.2 LIBS Experimental Setup	9
2.3 SIBS Experimental Setup	11
III. METHODOLOGY	14
3.1 Selection of Analyte Line for Hg Measurements	14
3.2 Spectral Background.....	16
3.3 Parametric Study.....	18
3.3.1 Effect of Excitation Energy on SIBS Signal.....	18
3.3.2 Effect of Gate Delay on SIBS Signal.....	19
3.3.3 Effect of Gate Width on SIBS Signal	22
3.3.4 Effect of Excitation Energy on LIBS Signal.....	24
3.3.5 Effect of Gate Delay on LIBS Signal	25
IV. ANALYSIS AND RESULTS.....	27
4.1 Data Analysis Method.....	27
4.1.1 Absolute Intensity	28
4.1.2 Intensity-to-Background Ratio.....	29
4.1.3 Mercury (Hg)-to-Iron (Fe) Ratio	29
4.2 SIBS Calibration	30
4.3 LIBS Calibration.....	33
4.4 SIBS and LIBS Comparison	35

4.4.1	Types of Sample	35
4.4.2	Spectra and Calibration.....	36
4.4.3	Limit of Detection.....	38
V.	CONCLUSION AND FUTURE DIRECTIONS.....	39
	REFERENCES	41
APPENDIX		
A.	CIRCUIT SCHEMATIC OF TRIGGERING SYSTEM AND HIGH VOLTAGE SYSTEM.....	44

LIST OF TABLES

3.1	Hg emission lines and its relative intensities from NIST Atom database [26].....	15
4.1	Summary of LIBS and SIBS operational parameters	38

LIST OF FIGURES

2.1	Pellet samples used in the LIBS experiment and powder sample used in SIBS experiment.	9
2.2	LIBS Experimental Setup	10
2.3	SIBS sampling system	12
2.4	SIBS Experimental Setup	13
3.1	Intensity of Hg emission lines.....	15
3.2	Spectra without placing a glass slide (above) and with a glass slide (below)	17
3.3	Effect of spark voltage on signal intensity.....	19
3.4	Effect of gate delay on SIBS Hg-to-background ratio.....	20
3.5	Relative standard deviation of Hg-to-background ratio with gate delay	21
3.6	Effect of gate delay on Hg signal intensity	21
3.7	Relative standard deviation of Hg intensity with gate delay	22
3.8	Effect of gate width on SIBS Hg-to-background ratio	23
3.9	Relative standard deviation of Hg-to-background ratio with gate width.....	23
3.10	Effect of laser energy on Hg signal intensity	24
3.11	Effect of gate delay on Hg-to- background ratio	26
3.12	Relative standard deviation of Hg-to-Background ration with gate delay	26
4.1	SIBS calibration with Hg intensity	31
4.2	SIBS calibration with Hg-to-background ratio	31
4.3	SIBS calibration with Hg-to-Fe intensity ratio	32

4.4	SIBS calibration with Hg-to-Fe peak area ratio.....	32
4.5	LIBS calibration with Hg intensity	33
4.6	LIBS calibration with Hg-to-background ratio.....	34
4.7	LIBS calibration with Hg-to-Fe intensity ratio.....	34
4.8	LIBS calibration with Hg-to-Fe peak area ratio	35
4.9	LIBS spectra (above) and SIBS spectra (below)	37
A.1	Circuit schematic of triggering system and high voltage system	45

CHAPTER I

INTRODUCTION

1.1 General Introduction

In today's society, many of our activities have resulted in the emission of metals into environment which has become one of the major sources of contamination. Most affected are soils due to emission of heavy metals like mercury (Hg), lead (Pb), and arsenic (As) [1, 2]. This pollution has become hazardous for both flora and fauna of the surroundings. The runoff water from these soils may even contaminate nearby water bodies with these metals. Thus to take necessary precautions and to proceed with remedial measures, continuous monitoring of the soils for the presence of these heavy metals has become essential. There are many established analytical laboratory techniques, such as atomic absorption spectroscopy (AAS), X-ray fluorescence (XRF), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), for the purpose of quantification [3-5]. They are considered to be efficient and also have good detection limits. Gaudiuso et al. [6] has recently reviewed these techniques with an emphasis on soil analysis. But the disadvantage of these techniques is that they are time consuming. The sample has to be meticulously prepared and the whole process is laborious. These aspects make these techniques not appropriate for real-time in situ monitoring of metal contaminants in soils. One of the existing techniques that is now in commercial use for in situ monitoring

involves the use of portable XRF instruments that were developed during the 1990's [7]. It has been observed that the results are largely affected due to matrix variation; thus obtaining correct quantitative results is hampered. Due to these factors, a need for an analytical technique which is robust, yet simple and portable arose.

Laser Induced Breakdown Spectroscopy (LIBS) is such a technique which is believed to overcome the limitations of established analytical techniques. The foundations of this technique were laid in the early 1980's and there has been a growing curiosity in the scientific community regarding its efficiency. Over the years, there has been significant research studying the capability of LIBS for quantification of metals in soils and encouraging results were obtained [8-10]. Though this technique is less mature than XRF or ICP-MS, the results are observed to be comparable to those of standard techniques. However, the fact remains that the plasma conditions generated in LIBS are difficult to exactly reproduce.

The working principle of LIBS is as following: a laser pulse strikes the surface of the material and some of the material is ablated. The ablated material is atomized, creating plasma that contains excited atoms and ions. When these excited atoms and ions are de-excited, characteristic emission lines are obtained which give information about the composition of the material. The emission lines consist of both atomic lines and ionic lines.

There is also another technique which generates plasma by the aid of sparks instead of lasers and which recently has also been used for analysis. This technique is known as Spark Induced Breakdown Spectroscopy (SIBS). This technique is developed by combining the principles of traditional spark spectroscopy and Laser Induced

Breakdown Spectroscopy (LIBS); hence it can be termed as a ‘marriage’ of these two pulsed plasma-generating techniques [12]. The principle of plasma generation is akin to LIBS. A spark generated between two electrodes ablates some sample material which is vaporized, atomized and excited. The characteristic emission lines are studied to determine the elemental composition of the sample. This technique has been applied to measure heavy metals in aerosols and soils and for fuel concentration measurement. [11-14].

In recent years, there has been growing interest in the scientific community to investigate and develop a better technique for the in situ monitoring of soils. Both LIBS and SIBS are being extensively put to use for quantitative analysis of heavy metal and trace elements in soils. The work of Senesi et al. [15] demonstrated that LIBS can be a potential technique for reliable qualitative and quantitative analytical evaluation for heavy metals in soils. Hussain et al. [16] used the LIBS technique for identification of barium and chromium in oil-spilled soils. There have been several studies and a large amount of literature is available indicating that the study of LIBS is a burgeoning field, particularly in the case of soil analysis. However there are several studies that question the efficiency of LIBS for quantitative analysis. Essington et al. [17] reports that correlations of LIBS responses with elemental contents are poor. Ismael et al. [18] reports that the LIBS technique still needs to be enhanced for quantitative analysis.

Although traditional spark spectroscopy has been used for over a long period of time, the recent usage of sparks to produce induced breakdown has revived interest in its application for spectroscopic analysis. The historical perspective and developments in spark emission spectroscopy can be learnt from the review of Walters [19]. As mentioned

earlier, there has been interest in developing SIBS as a low-cost alternative to LIBS, particularly for analysis of heavy metals in soils. SIBS was previously applied to aerosol metal monitoring [11] and obtained encouraging results. This method has also been used for monitoring heavy metals, such as Cr. LIBS and SIBS are both pulse discharges, but with quite different plasma characteristics. In this work, I investigated and compared these two potential techniques, Laser Induced Breakdown Spectroscopy (LIBS) and Spark Induced Breakdown Spectroscopy (SIBS), for the rapid monitoring of heavy metals in soils. For this purpose, I employed both these techniques for the quantification of mercury (Hg) in Oak Ridge, Tennessee, USA soil and the results are reported. The results from the SIBS experiment are compared with those obtained from Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The results reported here focus on univariate analysis, since this is just a comparative study of these two potential techniques. Obviously, employing robust chemometric techniques would give better results, but for the purpose of comparison, univariate analysis is sufficient.

1.2 Theoretical Background

LIBS and SIBS are both atomic emission-based techniques but they use different high energy excitation sources. LIBS uses a focused laser beam to form a plasma and SIBS uses a discharge source to produce an electrical spark. This section briefly addresses the theoretical background of plasma generation and the parameters that influence the analytical measurements and analysis of SIBS and LIBS. Though the physics of laser-induced or spark-induced plasmas is not completely understood, work in this area continues for a better understanding of laser- and spark- induced plasmas. The basic principle in both these techniques is the same, viz; using the plasma generated from

a high energy spark or laser source. The sample gets ablated, atomized and electronically excited. The excited atoms return to the ground state by emitting photons of characteristic frequency- a signature of a particular element. Though these techniques have an advantage over other analytical methods in terms of sample preparation, *in situ* analysis, rapid and real time analysis they are susceptible to variations in environment or in experimental parameters. This makes the reproducibility of the plasma difficult. The parameters that generally affect the measurements are energy and duration of the excitation source, shot-to-shot variations, and the detection window (i.e., the gate delay and gate width). It has been reported that the emission characteristics of laser-induced plasmas vary with the gaseous atmosphere surrounding the sample [20]. It has been observed that the signal intensity increases with laser energy, but when the laser energy is further increased, the signal seems to reduce due to self absorption while increasing the background [21]. This makes the selection of the excitation source energy important. Since SIBS and LIBS use pulsed sources to produce plasmas, the resulting spectra vary with time due to the transient properties of the laser (spark)-induced plasma plume. It has been observed, both in LIBS and SIBS, that the analyte line is accompanied by continuous background, caused by Bremsstrahlung emission and that the emission line and background decay at different rates. In the case of LIBS signal, in the 0-100 ns range, there is a huge background and no atomic lines are observed, while from 300-ns range, atomic lines can be observed accompanied with background; after 10 μ s atomic lines decay and molecular bands are observed [21]. Similar phenomena could be observed in spark-generated plasma on the μ s time scale [22]. Therefore by using a time-resolved detection system, an appropriate gate delay and gate width can be selected such that the

signal-to-background (S/B) ratio is optimum and the measurements are perfectly done. Also the selection of an analyte line is important as interference can affect the analytical measurements. The reasons for interference are the self-absorption, spectral overlap, matrix effects etc. Thus, the analyte line selected should be free of interference for intensity calculations. Depending on the wavelength of the laser and the density conditions, two mechanisms play a prominent role in generation and growth of electrons in the plasma. One mechanism is multiphoton absorption which is important in the case of shorter wavelength and low density. The electron density in the plasma grows linearly with time in this case. The other mechanism is collision induced ionization which is important under longer wavelength or high density conditions. The electron density in the plasma initially grows exponentially with time [21]. The analytical measurements are generally made after the plasma reaches Local Thermal Equilibrium (LTE) condition. At this condition, the intensity of the analyte line is proportional to the relative population of the level and obeys the Boltzmann distribution. Under the LTE condition, the intensity of the analyte emission line can be expressed as

$$I_{ji} = n(h\nu_{ji}) \frac{A_{ji}g_j}{Q(T)} e^{-hcE_j/kT} \quad (1.1)$$

where n is the density of the element, g_j is the statistical weight of the upper level, A_{ji} is the transition probability, $Q(T)$ is partition function at temperature T , h is Planck's constant, ν is the frequency of photon emitted when transition from higher to lower energy took place, c is velocity of light, E_j is the energy of the upper level, k is the Boltzmann constant, and T is the plasma temperature. This equation gives us the basis for developing a calibration model for analyte line intensity vs. concentration of the sample.

Based on this theoretical background, the optimum experimental conditions were determined and the calibration (for quantification of mercury in soils) was developed.

CHAPTER II

EXPERIMENTAL

2.1 Sample Preparation

The soil samples were analyzed in either powder or pressed pellet forms. A finely ground soil sample from Oak Ridge, TN, USA was used in this work. To prepare samples with different Hg concentrations, the finely ground and filtered soil sample was mixed with appropriate amounts of HgS powder. The prepared soil powder samples were directly used for the SIBS measurements. The samples used for LIBS were in pellet form. Rosenwasser *et al.*, Martin *et al.*, and Krasniker *et al.* have reported that the RSDs (Relative Standard Deviations) of data from pellets were much smaller than those of data taken using the powder form [20-22]. Thus for this experiment, soil samples in pellet form were considered for better signal intensity. The standard samples were prepared in the following way. Five grams of soil sample with the required concentration of mercury (Hg) was finely ground and 0.4 ml of 2% polyvinyl alcohol binder was added to this. The sample was placed inside a die and a pressure of 3000 psi was applied to it for 10 minutes. The pellet was then heated for 30 seconds at 90⁰C to remove excessive moisture and to insure that the sample was completely dried. The concentration of mercury (Hg) in the soil samples used for the SIBS experiments ranged from 200 parts-per-million to 1000 parts-per-million while for the LIBS experiment the concentrations varied from 500 parts-per-million to 10000 parts-per-million.

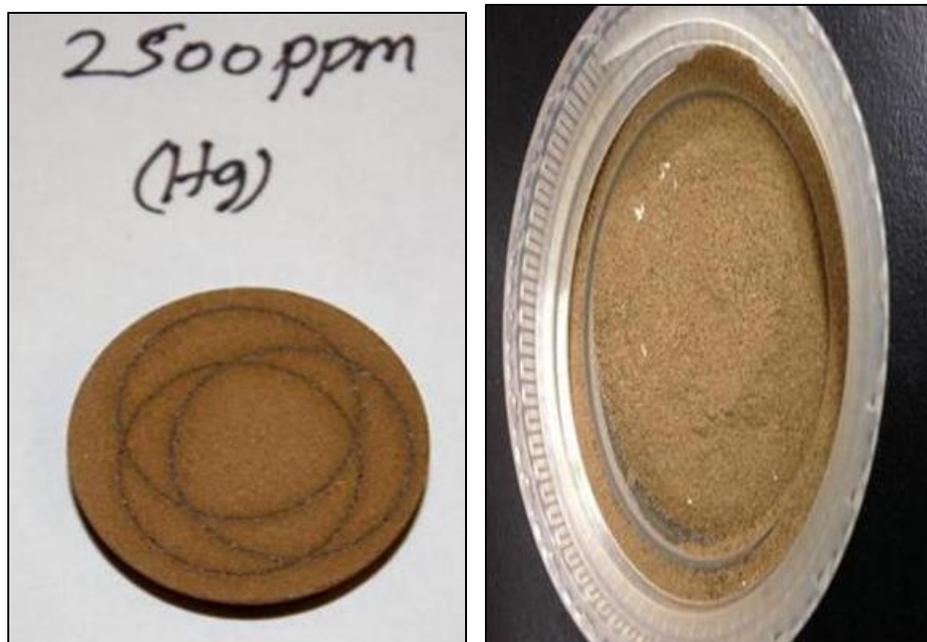


Figure 2.1 Pellet samples used in the LIBS experiment and powder sample used in SIBS experiment.

2.2 LIBS Experimental Setup

LIBS soil experiments were conducted using a frequency-doubled, Q-switched Nd:YAG laser (Big Sky Laser, 10 Hz, 8-ns pulse width, 9-mm diameter, 300 mJ maximum) as an excitation source. The laser was focused onto the sample (in the pellet form) using a 30-cm focal length converging lens made of fused silica. The signal from the laser-induced plasma was collected using a pick-up lens aligned at 45° angle with respect to the laser beam and transported into a 100- μm diameter optical fiber. The collected signal was sent into a spectrometer (Instruments SA (Jobin-Yvon) HR460) equipped with a 1024x256 intensified charged coupled device (ICCD) detector (Princeton Instruments). A programmable function generator (PG 200) triggered by the laser Q-switch was used to trigger and synchronize the ICCD camera. It provided the desired gate

delay time and width for the ICCD camera. Data acquisition and analysis were done using WINSPEC software version 2.1 A. Each spectrum was recorded with ten accumulations and ten spectra were collected for each sample to obtain a better signal-to-noise ratio for developing a calibration model for mercury (Hg). The LIBS sampling system and schematic of experimental setup are as shown in Figure 2.2.

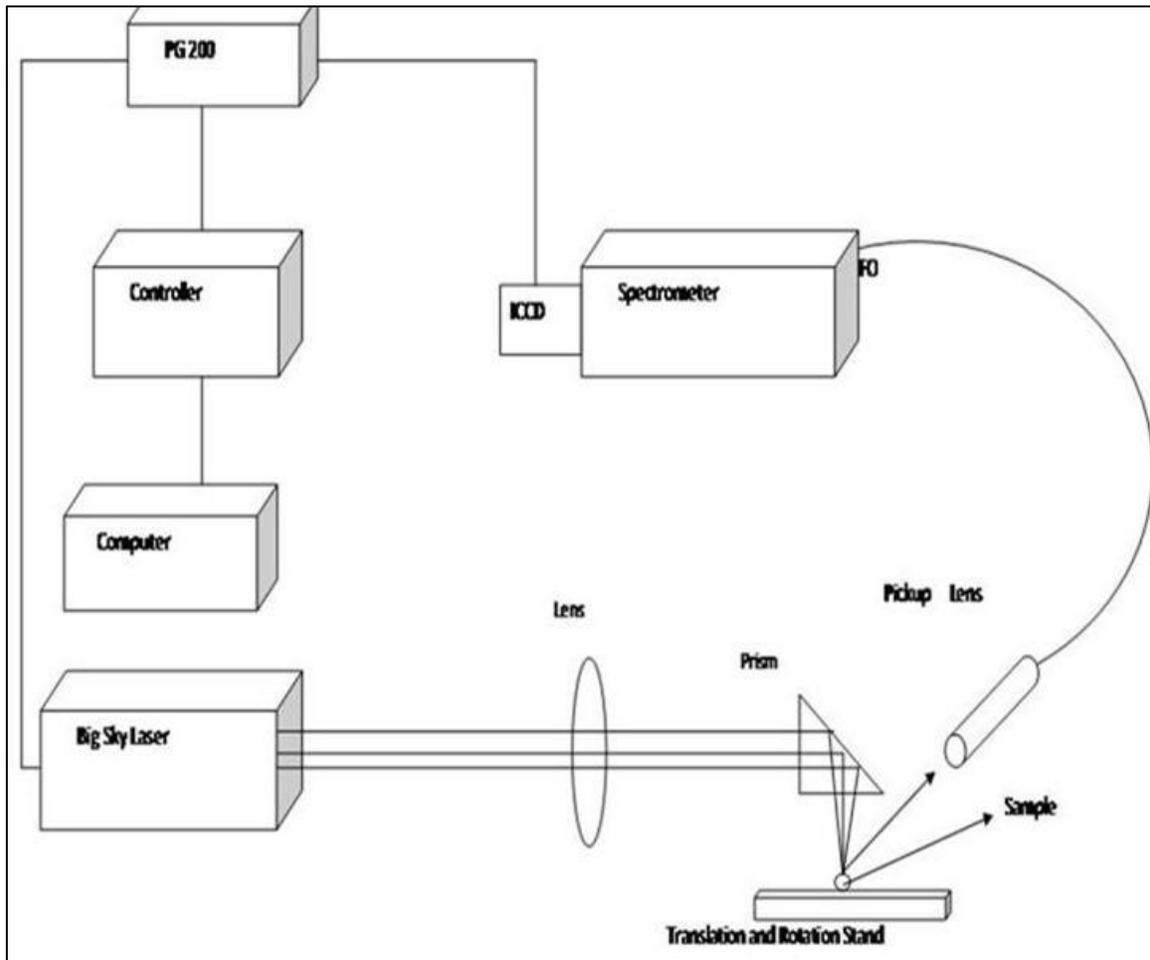


Figure 2.2 LIBS Experimental Setup

2.3 SIBS Experimental Setup

A home-made SIBS system was used in this work. The sample to be analyzed was placed on a Plexiglass insulator plate. The spark gap consisted of two 99.95% tungsten cylindrical rods of 3.2-mm diameter, placed ~5 mm apart. The two electrodes were mounted on two specially designed Plexiglass holders which allowed flexible adjustment of the electrode separation and position of the electrode tip. The electrodes were placed into the powder sample in a plastic container during the measurement. A high-voltage, low-current pulse generator initiated an ion channel between the spark gap. The ignition spark was triggered by a pulse generator (Heath 1277) to produce the ignition of sparks at 2.5 Hz. A high voltage (HV) power supply (Spellman SLM3P600, 3kV, 200mA) supplied high voltage to the spark generator to produce a high-current main spark through the charged capacitor bank discharge between the electrodes. The SIBS experimental setup is shown in Figure 2.2. The signal from the spark-induced plasma was collected by a pick-up lens placed above the two electrodes and was sent into a detection system used in LIBS setup (Instruments SA (Jobin-Yvon) HR460 spectrometer equipped with a 1024x256 intensified CCD detector). A programmable function generator PG 200 (Princeton Instruments) triggered by the spark generator was used to trigger and synchronize the ICCD camera. It provided the desired gate delay time and width for the ICCD camera. For the operation with the Princeton ICCD cameras ST133 controller (Princeton Instruments) is used. The function of the controller is the conversion of the analog data (the image data taken by the camera) to digital data. This controller is highly compatible with popular computer platforms and software packages; the data is transferred directly to the host computer memory through a high-speed serial link. Data

acquisition and analysis were done using WINSPEC software version 2.1 A. Each spectrum was recorded with twenty accumulations and ten spectra were collected for each sample for developing a calibration for mercury (Hg) in soil. The same detector was used for both SIBS and LIBS for a better comparison among the two techniques. The SIBS sampling system and the schematic of the SIBS setup were as shown in Figures 2.3 and 2.4.

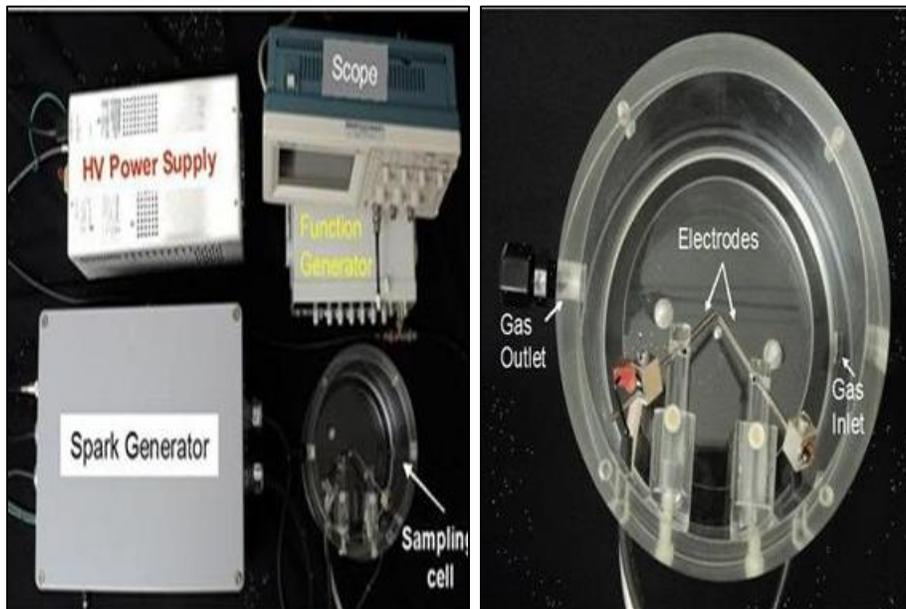


Figure 2.3 SIBS sampling system

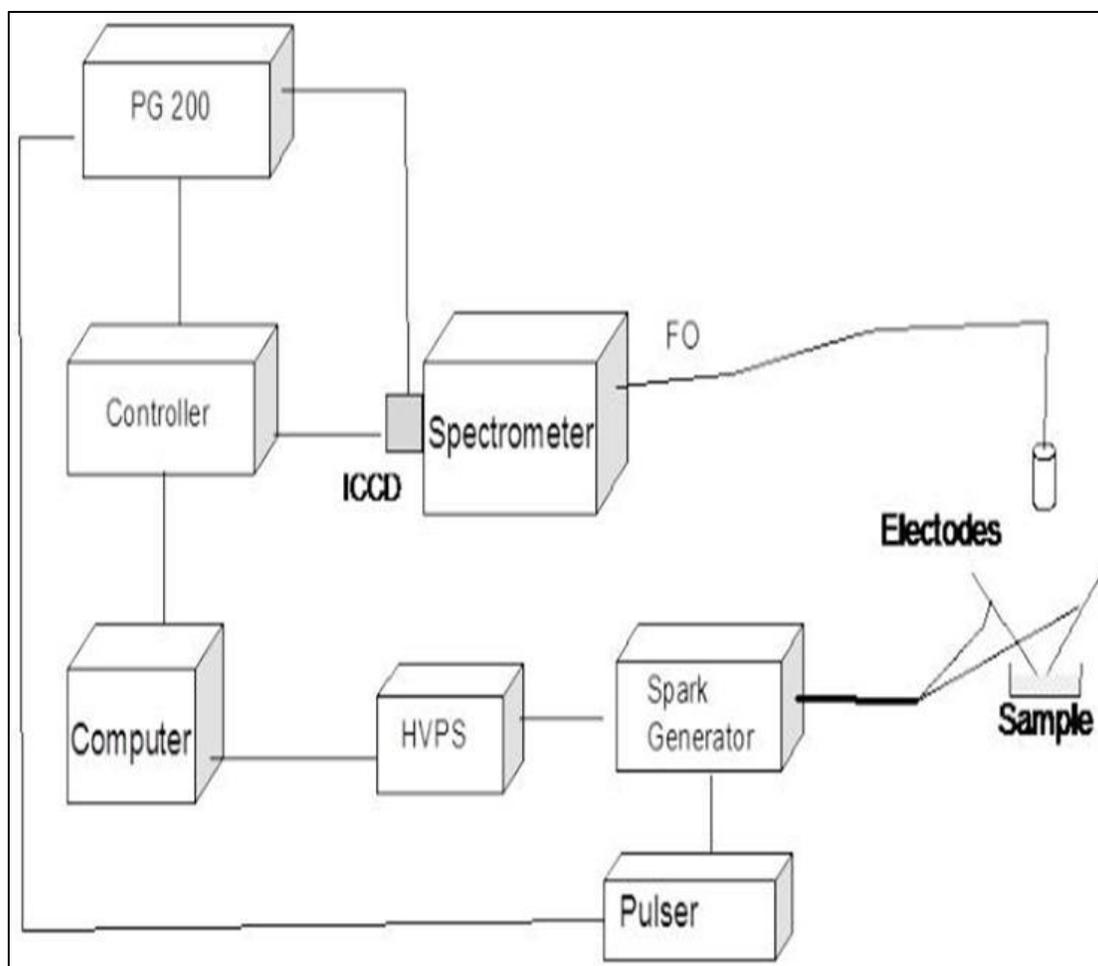


Figure 2.4 SIBS Experimental Setup

CHAPTER III

METHODOLOGY

To develop LIBS or SIBS as an analytical tool, the main issues are the precision and accuracy of the measurement. In this chapter, the various parameters that are important to optimize the LIBS and SIBS system are discussed below.

3.1 Selection of Analyte Line for Hg Measurements

The possible mercury emission lines for the Hg measurement are given in Table 3.1 [26]. Typically strong emission lines are used as analyte lines for trace element measurement. The strongest *mercury emission line* at 253.65 nm has been used in some previous LIBS work [27-28]. Recently, Gleason and Hahn have observed that the 253.7-nm mercury emission line is selectively quenched by oxygen species that are formed during the plasma recombination process [29]. Cheng did not observe the Hg 253-nm line in LIBS spectra of an aerosol. Hence the Hg 435-nm line was used instead. Hunter *et al.* have performed SIBS for measuring heavy metals in soils [30]. They chose the Hg 546.074 nm line as the analytical line for Hg. To select the analyte line for mercury measurement in soil in this work, LIBS spectra of soil that contain high concentrations of Hg were recorded to study possible spectral interferences. The intensity of Hg emission lines from LIBS spectrum are shown in Figure 3.1. The Hg line at 546.074 nm was found to have less spectral interference and hence this emission line was used for both LIBS

and SIBS measurements. The table below shows the various emission lines and their corresponding relative intensities.

Table 3.1 Hg emission lines and its relative intensities from NIST Atom database [26]

Hg line (nm)	Rel. Int.*
253.652	15000
365.015	2800
404.656	1800
435.833	4000
546.074	1100

* Relative intensities are source dependent and typically are useful only as guidelines for low density sources.

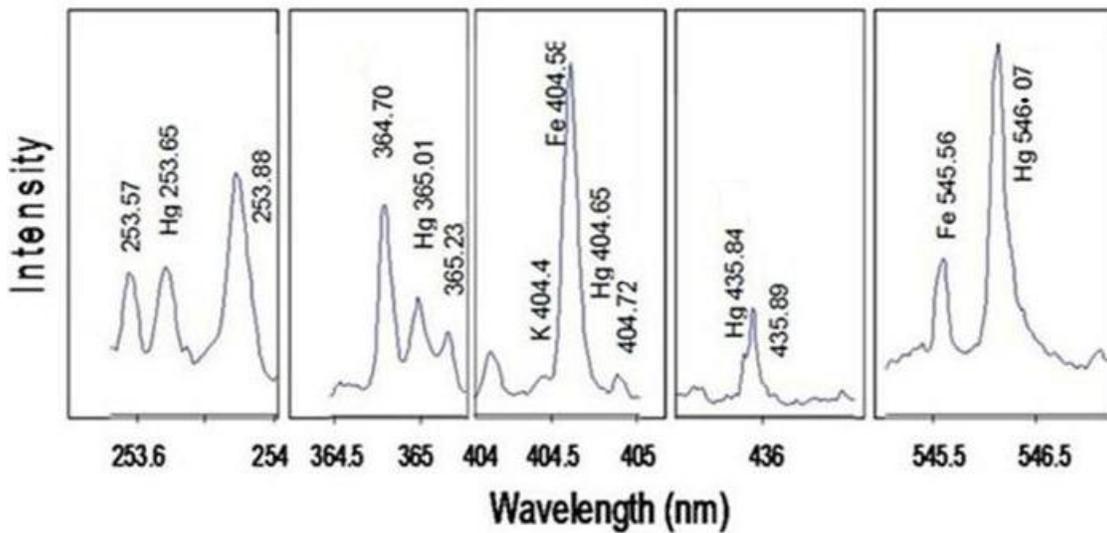


Figure 3.1 Intensity of Hg emission lines

3.2 Spectral Background

The detection of LIBS (SIBS) signal at a given wavelength will be the sum of the emission signal of the analyte, the emission signal of plasma continuum, and the detector (dark current). Spectral background can significantly affect signal-to-noise (S/N) and signal-to-background (S/B) ratios and affect the results of quantitative measurement. Therefore, during the process of optimization of a LIBS (SIBS) experiment, it is important to discriminate the spectral background. The continuous background in LIBS and SIBS decay with time, therefore by performing time-resolved measurements, it is possible to improve signal-to-background S/B and signal-to-noise S/N ratio. This section will discuss the parameters that affect time-resolved measurement in detail.

With the current detection system, I found that the signal from the second-order iron (Fe) lines and the background was high and it distorted the spectral region of interest (near Hg 546 nm). To optimize S/B and S/N ratios, it is necessary to discriminate the second order spectra, to minimize the second-order Fe lines and background, a glass slide was placed between two optical fibers that coupled the collected signal to HR-460 Spectrometer. As a result, the effect of the second order Fe lines is minimized and also the spectrum was observed to be smoother compared to that with no glass slide. The spectra obtained using a glass slide and without a glass slide is shown in Figure 3.2. So, for all the SIBS and LIBS observations, the glass slide was placed between the optical fibers in order to absorb ultraviolet light.

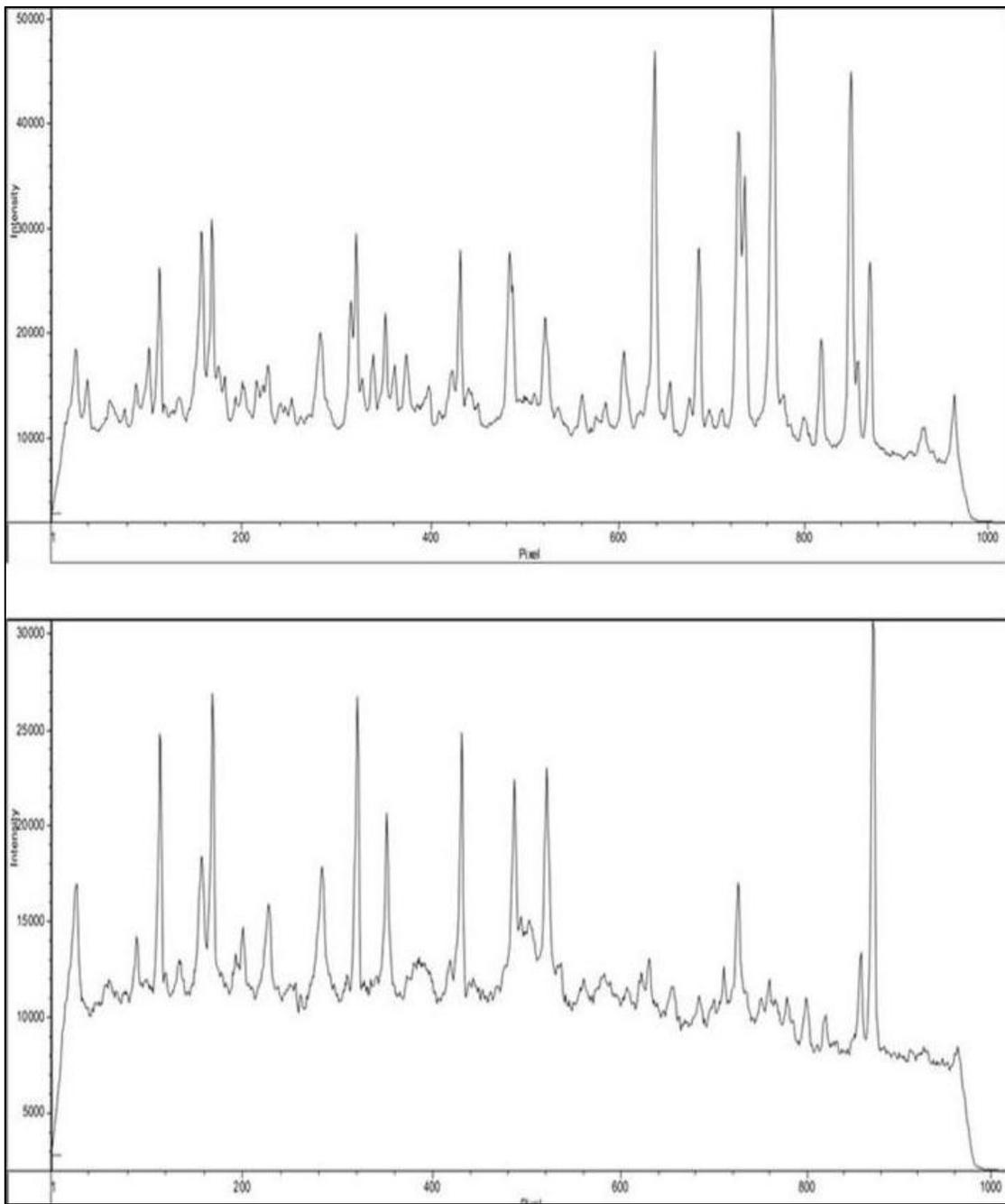


Figure 3.2 Spectra without placing a glass slide (above) and with a glass slide (below)

3.3 Parametric Study

LIBS and SIBS are pulsed discharges whose plasma parameters (i.e., plasma temperature, electron density, plasma volume, etc.) vary with time. The spark-induced plasma is affected by discharge voltage and current, pulse frequency, atmospheric pressure, and distance from the sample while the laser-induced plasma characteristics are dependent on laser irradiance, laser wavelength, pulse duration, target material, atmospheric conditions, space and time. For better quantitative measurements with transient plasmas, such as LIBS and SIBS, time-resolved emission spectra were recorded to obtain optimum experimental conditions for analytical measurements. The effect of gate delay, gate width and excitation energy on SIBS and LIBS are discussed below.

3.3.1 Effect of Excitation Energy on SIBS Signal

As mentioned in the section of theoretical background, the excitation energy plays an important role in analytical measurements. To study the influence of excitation energies on SIBS signals, at constant gate delay, the high voltage supplied to the charged capacitor bank was varied. The gate delay for the SIBS experiments was maintained at 20 microseconds and the gate width was maintained at 50 μ s. The spark voltage was varied from 0.5 kV to 2 kV; its effect on the signal intensity was observed and is shown in Figure 3.3. In this work, we have typically used 1 kV spark voltage for the SIBS study.

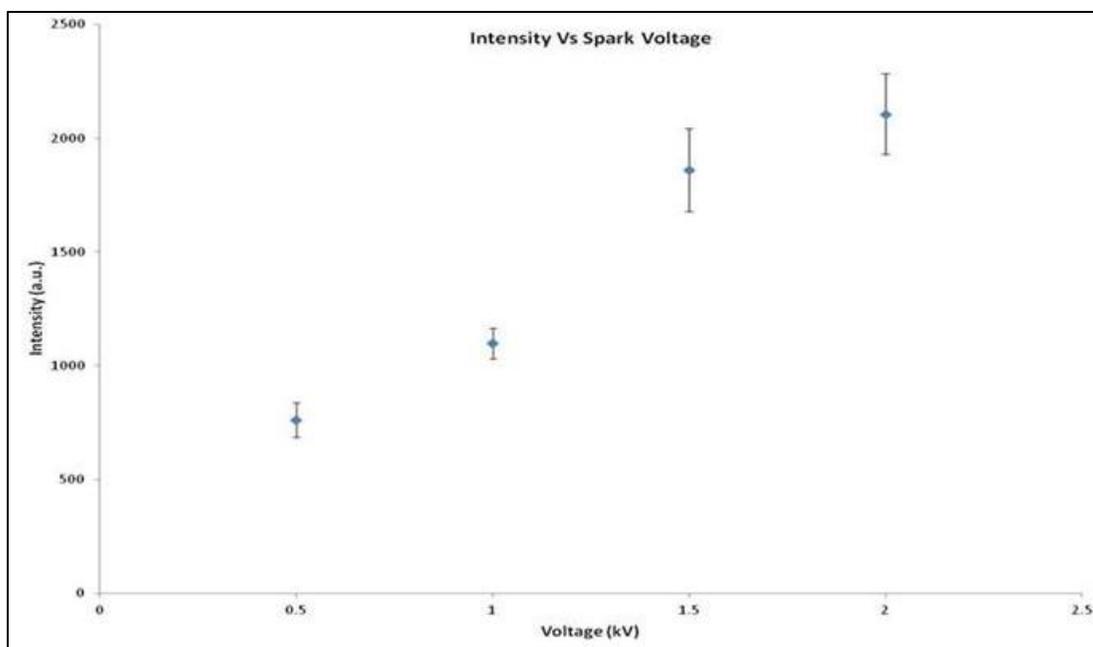


Figure 3.3 Effect of spark voltage on signal intensity

3.3.2 Effect of Gate Delay on SIBS Signal

As mentioned earlier, to ensure that the system does not get damaged, the spark voltage was fixed at 1kV and the spark frequency at 2.5 Hz. For obtaining an optimum condition for gate delay for SIBS experiments, a 1000-ppm (Hg) soil sample was used. The slit width of the spectrometer was maintained at 200 μm . The gate width was adjusted to 50 μm , the micro channel plate (MCP) voltage was kept at 600 V and exposure time was 0.5 sec. Spectra were collected using the WINSPEC software. The gate delay was varied from 1 μsec to 70 μsec and the variation of signal was observed. Five spectra, each of 10 accumulations were collected at each gate delay. The signal of Hg at 546.07 nm line was observed and analyzed to determine the optimum gate delay for SIBS. The signal-to-background ratio and the relative standard deviation (RSD) of the

analyte line recorded at constant excitation energy were used to determine the optimum detection window for signal detection. Relative standard deviation is useful in comparing the spread of observations from the average value. It is obtained by dividing the standard deviation by the average. It has been observed that at 40 μ second gate delay the SIBS signal was observed to have maximum signal-to-background ratio with minimum relative standard deviation. These gate delays were used in developing the calibration model for mercury in soils. The effect of gate delay on SIBS signal is as shown in Figures 3.4 to 3.7.

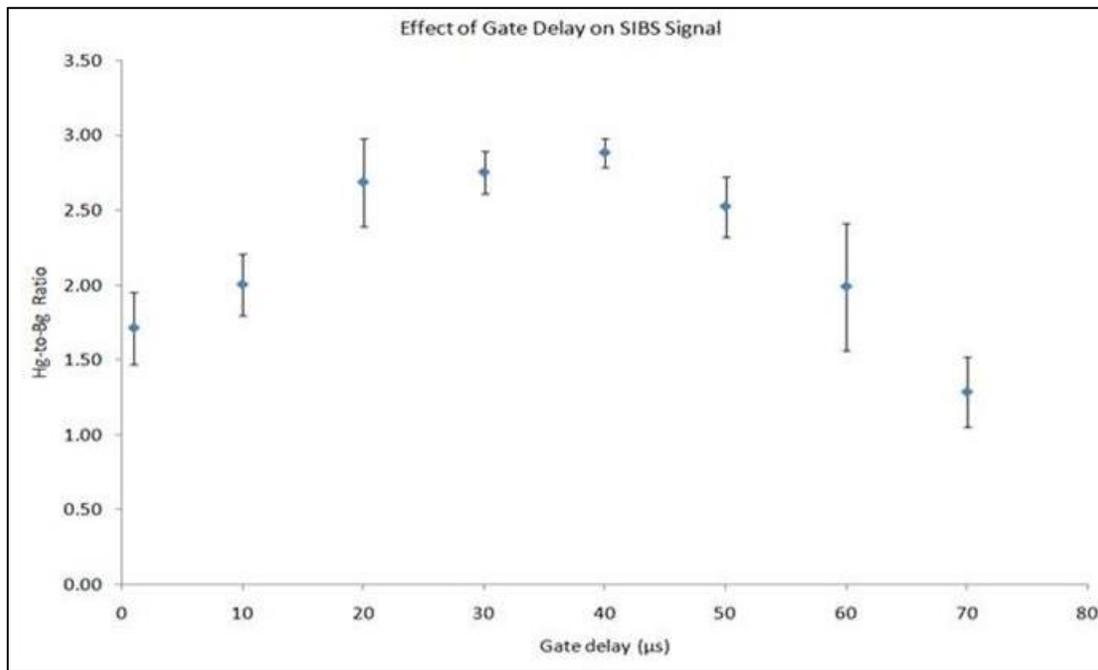


Figure 3.4 Effect of gate delay on SIBS Hg-to-background ratio

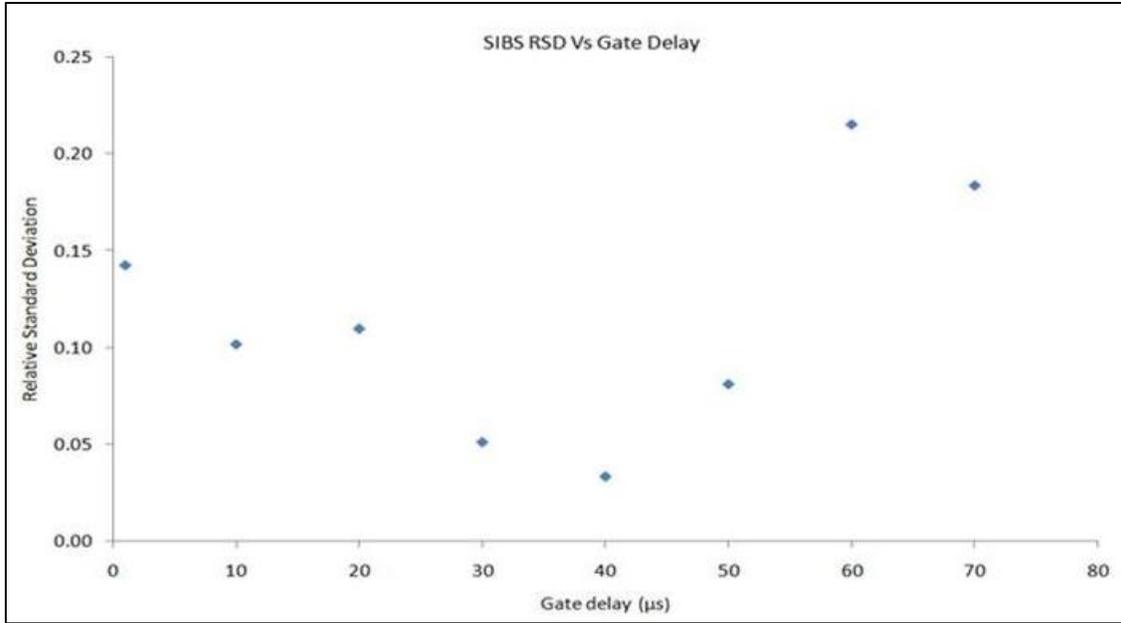


Figure 3.5 Relative standard deviation of Hg-to-background ratio with gate delay

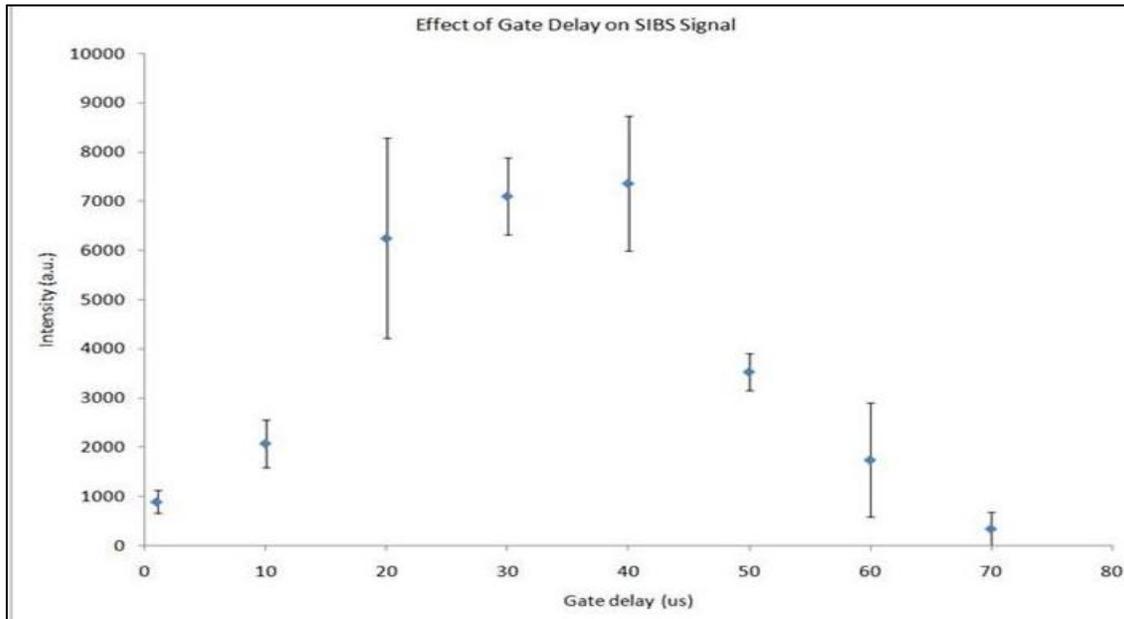


Figure 3.6 Effect of gate delay on Hg signal intensity

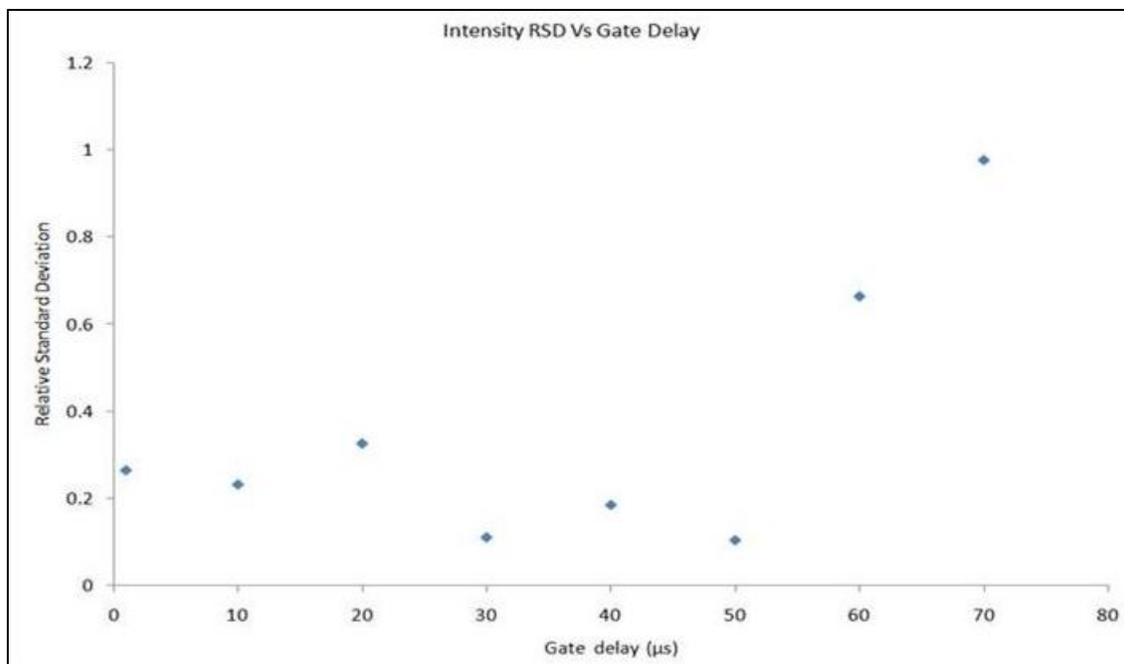


Figure 3.7 Relative standard deviation of Hg intensity with gate delay

3.3.3 Effect of Gate Width on SIBS Signal

The high voltage was maintained at 1kV and gate delay was fixed at 40 μs . The gate width was varied from 50 μs to 700 μs . The ratio of mercury analyte line to background was observed to determine the optimum gate width. It was observed that 50 μs gate width has good signal-to-background ratio. Hence this gate width was used in obtaining calibration model for SIBS technique. The effect of gate width on SIBS signal is as shown in Figure 3.8 to 3.9.

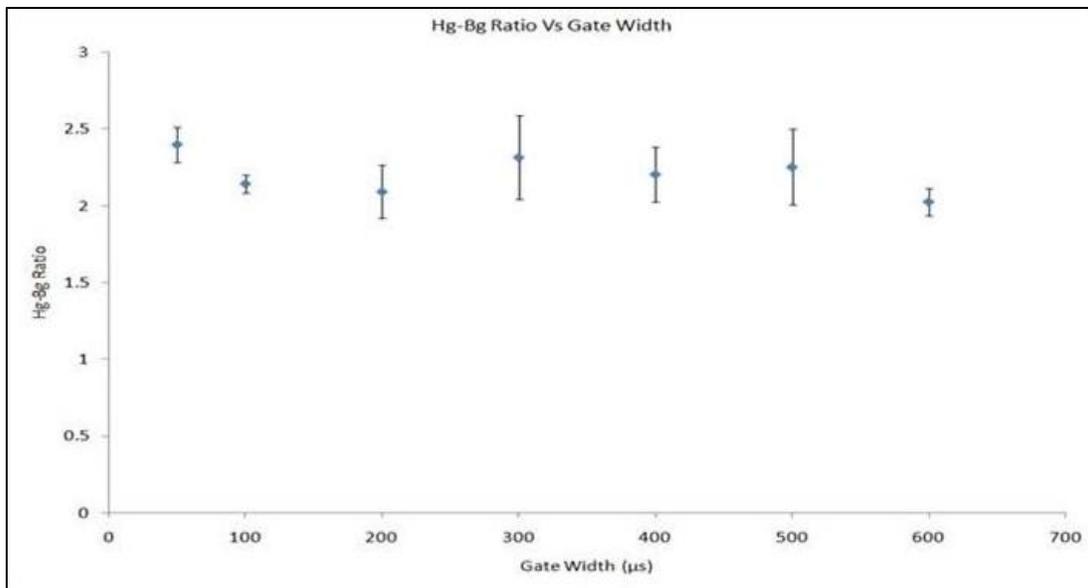


Figure 3.8 Effect of gate width on SIBS Hg-to-background ratio

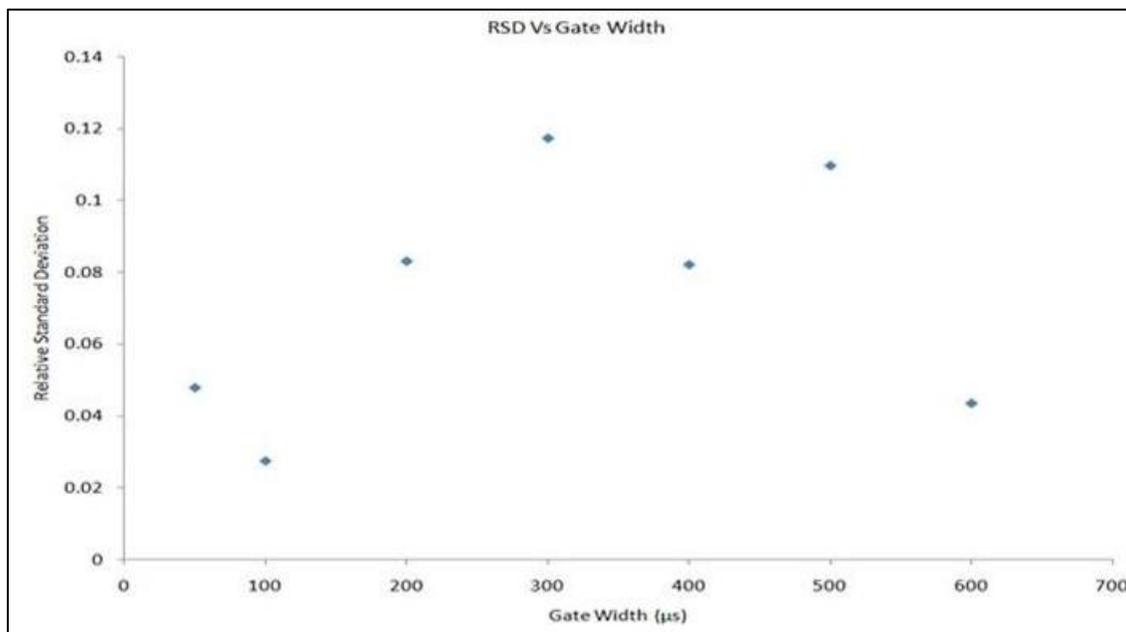


Figure 3.9 Relative standard deviation of Hg-to-background ratio with gate width

3.3.4 Effect of Excitation Energy on LIBS Signal

To study the influence of excitation energies on LIBS signal at constant gate delay, the variation in signal intensity of the analyte line with the laser pulse energy was observed. The gate delay for the LIBS experiments was maintained at 0.5 microseconds and the laser energy was varied. It was found that the signal increases as the excitation energy was increased until it reach saturation at certain energy and then the intensity reduces. The intensity of Hg analyte line increased and was maximum at 62.5 mJ. At higher energies the intensity reduced and it was also observed that significant amount of sample was being ablated from the pellet and spilling on to the apparatus. Since we were working with high concentrations of mercury in the samples, considered the safety, the energy of laser pulse was chosen to be 62.5 mJ per pulse. The variation of signal intensity with laser energy is as shown in the Figure 3.10.

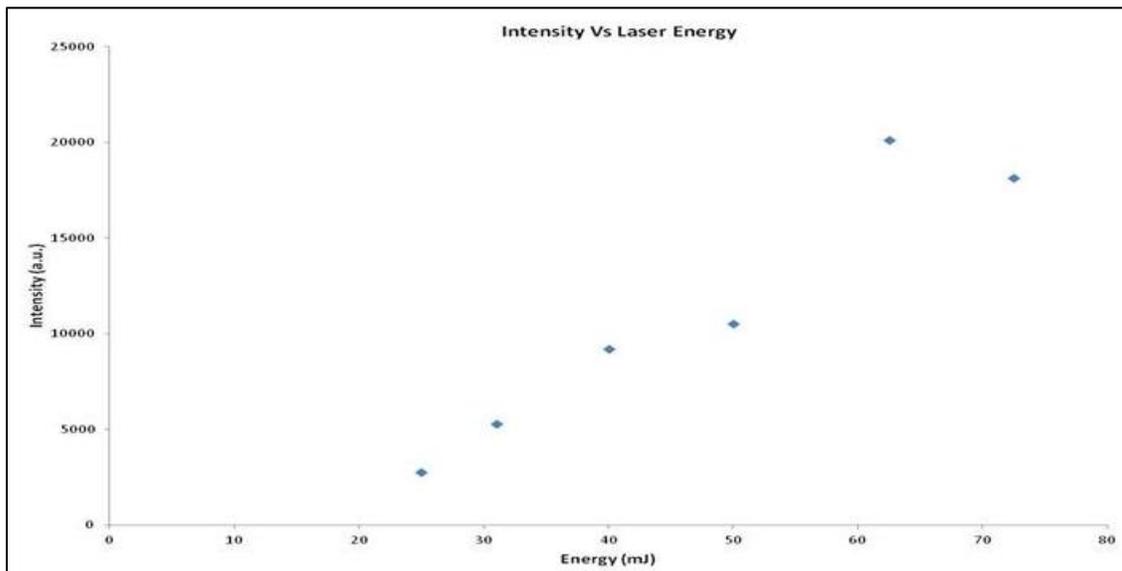


Figure 3.10 Effect of laser energy on Hg signal intensity

3.3.5 Effect of Gate Delay on LIBS Signal

For the LIBS measurements, nanosecond laser was used. LIBS spectra of soil sample in pellet form with gate delays from 400 ns to 1500 ns were recorded. The laser energy was maintained at 62.5mJ/pulse; gate width was adjusted to 5 μ sec, exposure time of 0.5 sec was used and MCP voltage was 800 Volts. The signal of Hg at the 546.07 nm analyte line was observed. The spectra were analyzed and the optimum gate delay for LIBS was determined. This gate delay was used in developing the calibration for mercury. The signal-to-background ratio and the relative standard deviation of the analyte line recorded at constant excitation energy were used to determine the optimum detection window for signal detection. LIBS signal intensities initially increase with increasing gate delay, reach a maximum, and then decrease. It was observed that at 1 μ sec gate delay the Hg-to-background ratio was observed to be maximum with minimum relative standard deviation. Thus the gate delay of 1 μ sec was used for developing calibration model for LIBS technique. The effect of gate delay on LIBS signal is as shown in the Figures 3.11 and 3.12.

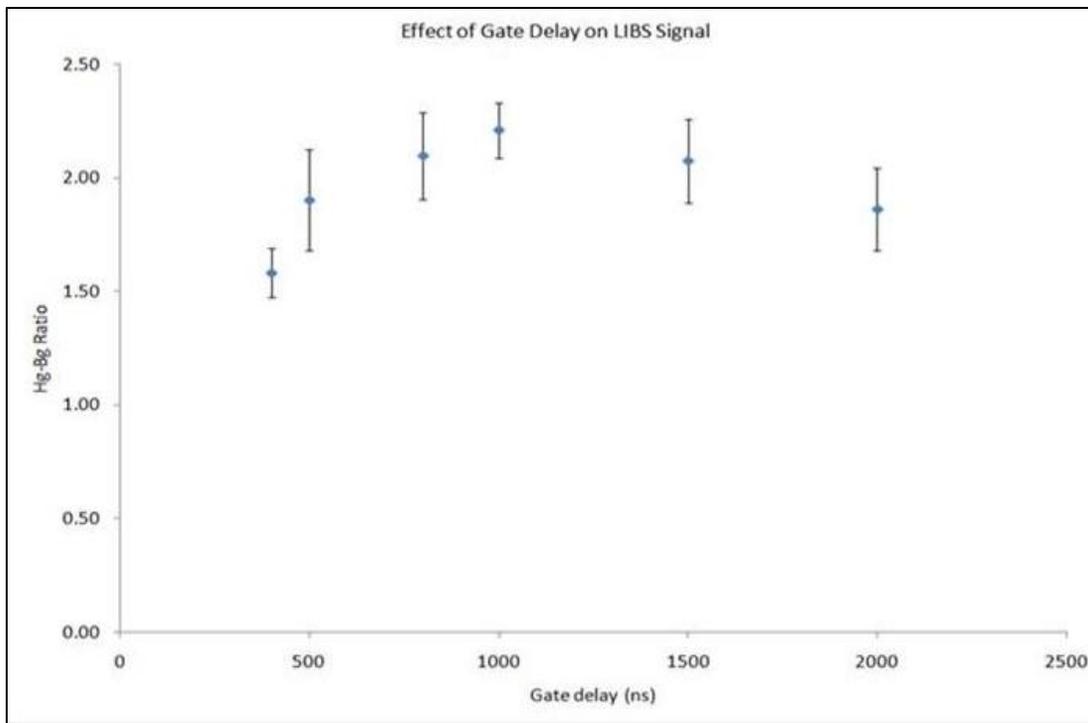


Figure 3.11 Effect of gate delay on Hg-to- background ratio

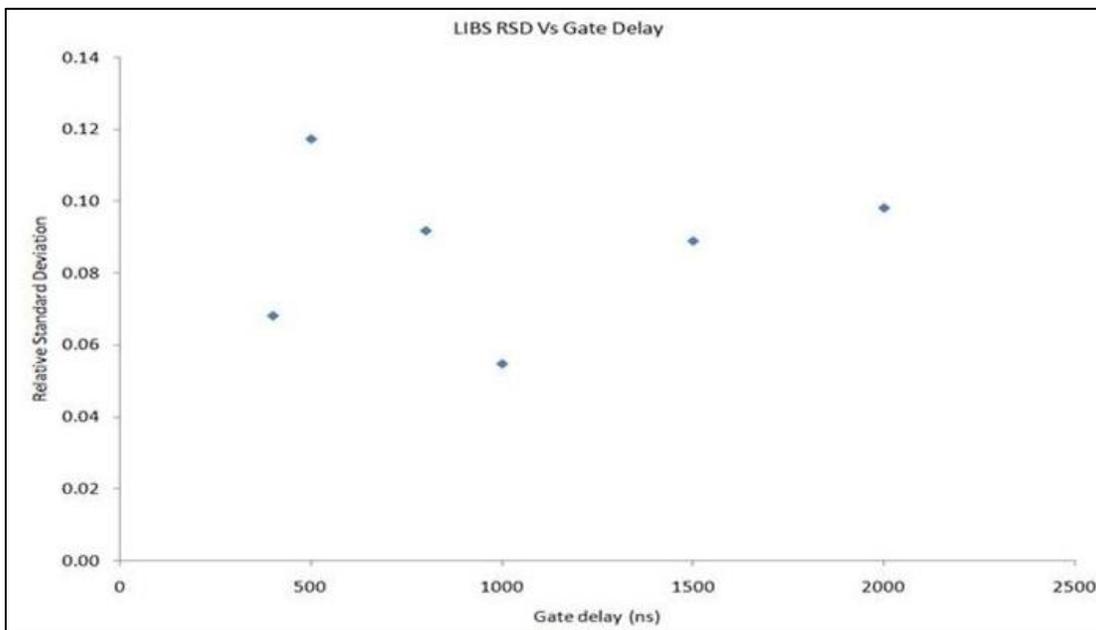


Figure 3.12 Relative standard deviation of Hg-to-Background ration with gate delay

CHAPTER IV

ANALYSIS AND RESULTS

4.1 Data Analysis Method

The Hg analyte line considered in this analysis is 546.07 nm. For both SIBS and LIBS analyses, the data acquired using WINSPEC software was saved in ACII format for the purpose of analysis. A 2400 line/mm grating was used for recording spectra which gives a wavelength range of about 16 nm. The wavelength was centered at 546.07 nm and thus the spectra were obtained in the wavelength region from 537.919 nm to 553.779 nm. As mentioned in the introduction, the results reported in this section are based on univariate analysis of the data where a single emission line is considered for the analysis. Five sets of data for both SIBS and LIBS were collected and used in the analysis. The methods applied to develop the calibration model for SIBS and LIBS are the a) absolute intensity b) mercury (Hg)-to-background intensity ratio c) Hg-to-Fe intensity ratio and d) Hg-to-Fe area ratio. For the ratio calculation the Fe emission line chosen was the 544.69nm analyte line. From the calibration curve, the line intensity measured for an unknown sample can be compared to estimate the concentration of the unknown sample. This approximation can be considered valid if all other parameters affecting the plasma characteristics are constant during the calibration and measurement [8]. Both SIBS and LIBS spectra contains large and complex information regarding the composition of the sample which is used for both qualitative and quantitative analysis. Therefore selecting a

suitable data analytical method to analyze the sample is of importance. Most researchers use the univariate data analysis approach [23, 31-33] to analyze LIBS and SIBS spectra. The univariate approach is a technique where a single emission line of the element of interest is considered for analysis. The calibration model developed is of the form

$$Y = mX + C \quad (4.1)$$

where X (independent variable) is the concentration of element in the sample, Y (dependent variable) is the peak intensity or intensity ratio and C is the offset. The limit of detection is calculated using the International Union for Pure and Applied Chemistry (IUPAC) definition

$$LOD = 3\sigma/m \quad (4.2)$$

where σ is the standard deviation of the background and m is the slope of the calibration curve obtained.

In the present study, based on the theoretical background, the optimum experimental conditions for SIBS and LIBS were determined and with these parameters, spectra from calibration samples were obtained. The univariate data analysis approach was applied to the obtained spectral data to analyze and compare SIBS and LIBS techniques for quantification of mercury in soils.

4.1.1 Absolute Intensity

The absolute intensity of the analyte line is calculated by subtracting the peak height from the background signal near the analyte line. The calibration model is developed for quantification of mercury using the absolute intensity values vs. concentration of mercury in the sample. This method is applied for both SIBS and LIBS

spectra and it has been observed that the RSD values are high. The limits of detection (LOD) for SIBS and LIBS were calculated from the absolute intensity vs. concentration plot. To reduce the RSD values, other ratio methods are employed to develop the calibration model.

4.1.2 Intensity-to-Background Ratio

Intensity-to-background ratio was obtained by calculating the ratio of the peak height of the analyte line to the average background intensity in the vicinity of the analyte line. It has been observed during the SIBS experiment that in some cases each spectrum had a different background. This variation might be due to the change in the electrode separation distance (due to the pressure from spark, the distance between the electrodes might vary) or that the surface may not have enough sample to create a plasma. In such conditions, absolute intensity may not give an accurate calibration model. Hence Intensity-to-background ratio method was employed. This method was also used in LIBS calibration for the purpose of comparison. This method resulted in smaller values of RSD compared to absolute intensity values.

4.1.3 Mercury (Hg)-to-Iron (Fe) Ratio

Mercury (Hg) to iron (Fe) intensity ratio was obtained by calculating the ratio of the peak height of the Hg 546.07-nm line to the peak height of the Fe 544.69-nm line. This method was applied for both SIBS and LIBS for developing the calibration model. Mercury (Hg) –to- iron (Fe) peak area ratio was also obtained by calculating the ratio of peak area of the Hg 546.07-nm line to the peak area of Fe 544.69-nm line and a calibration model was developed.

4.2 SIBS Calibration

After obtaining the optimum values for the parameters, a calibration model for mercury (Hg) in soils using SIBS was to be developed. To obtain the calibration model for low concentrations of mercury using SIBS, five standard soil samples containing Hg concentrations of 200 ppm, 400 ppm, 600 ppm, 800 ppm and 1000 ppm were used. The spectra were acquired, analyzed and a calibration model was developed by applying the methods discussed above. The calibration curves, regression values (R^2) values are as shown in the Figures 16 to 19. For SIBS, it has been observed that the calibration model developed using the Hg-to-background ratio is observed to be more linear and smaller relative standard deviation compared to those of absolute intensity. The R^2 value for the absolute intensity calibration was observed to be 0.997 with a RSD of about 19% for the lowest concentration sample. It was calculated to be 30% at 1000 ppm. The R^2 value for Hg-to-background ratio calibration was observed to be 0.999 with RSD of 1% at 200 ppm and about 5% at 1000 ppm. The limit of detection was calculated using the IUPAC definition $LOD = 3\sigma/m$ where σ is the standard deviation of background and m is the slope obtained from the absolute intensity vs. concentration calibration. The LOD using SIBS for mercury in soil was calculated to be 20 ppm.

The calibration developed for quantification of mercury in soils using the above stated methods is as shown in Figures 4.1 to 4.4

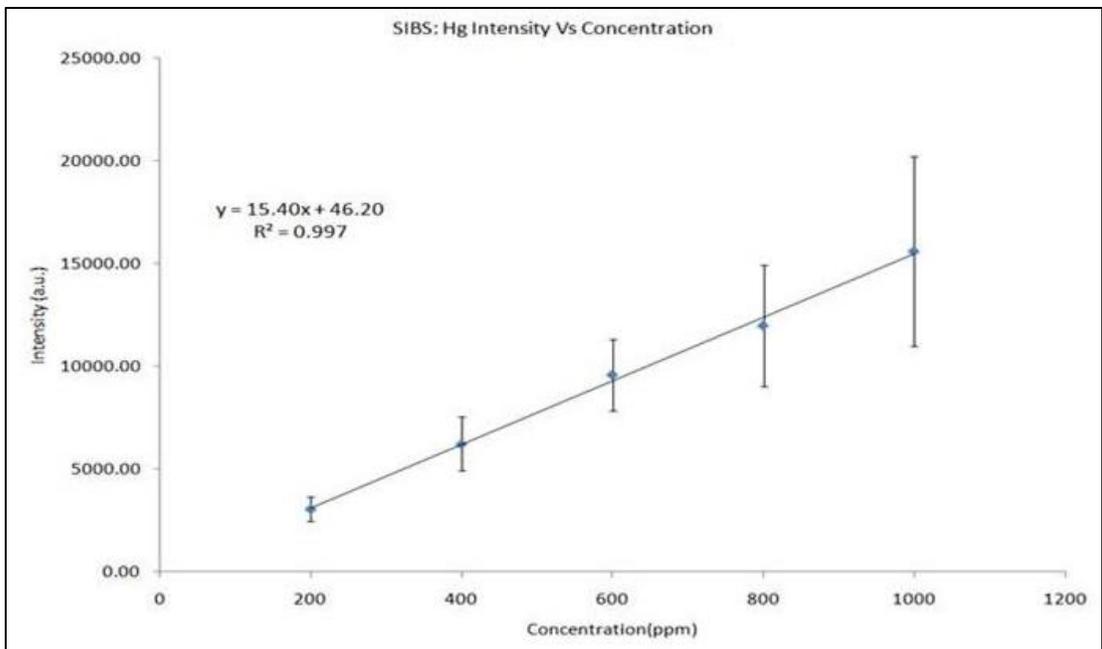


Figure 4.1 SIBS calibration with Hg intensity

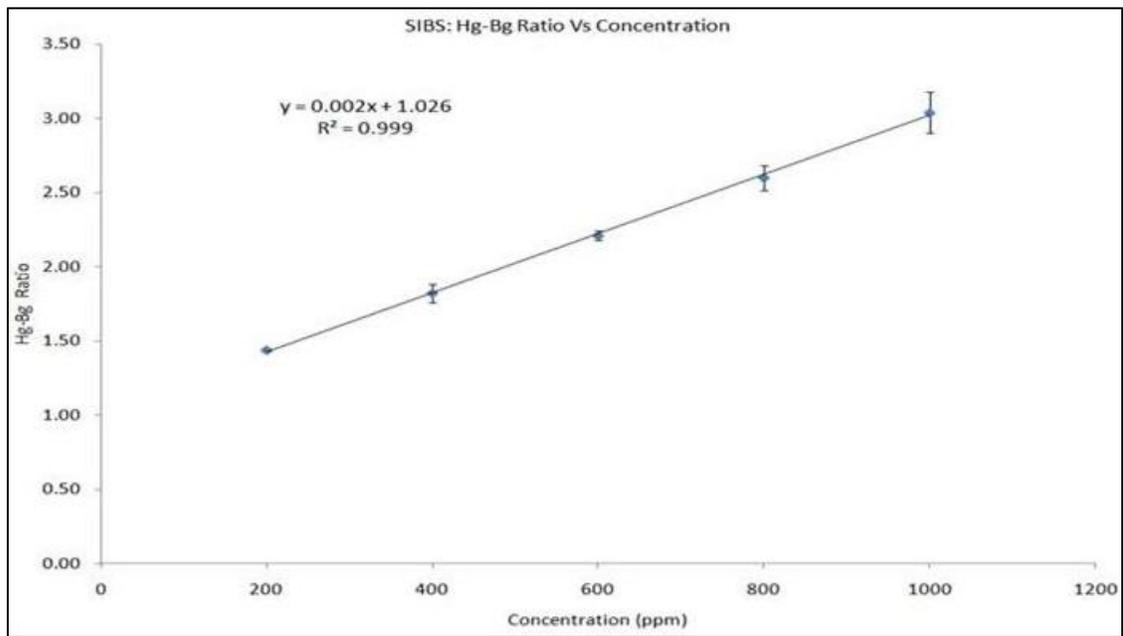


Figure 4.2 SIBS calibration with Hg-to-background ratio

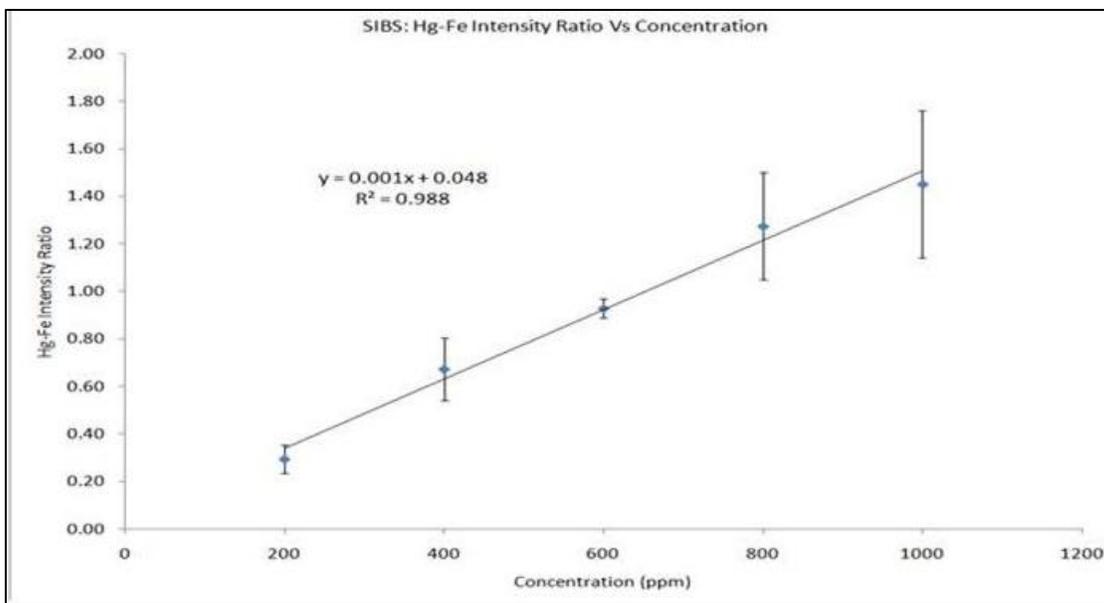


Figure 4.3 SIBS calibration with Hg-to-Fe intensity ratio

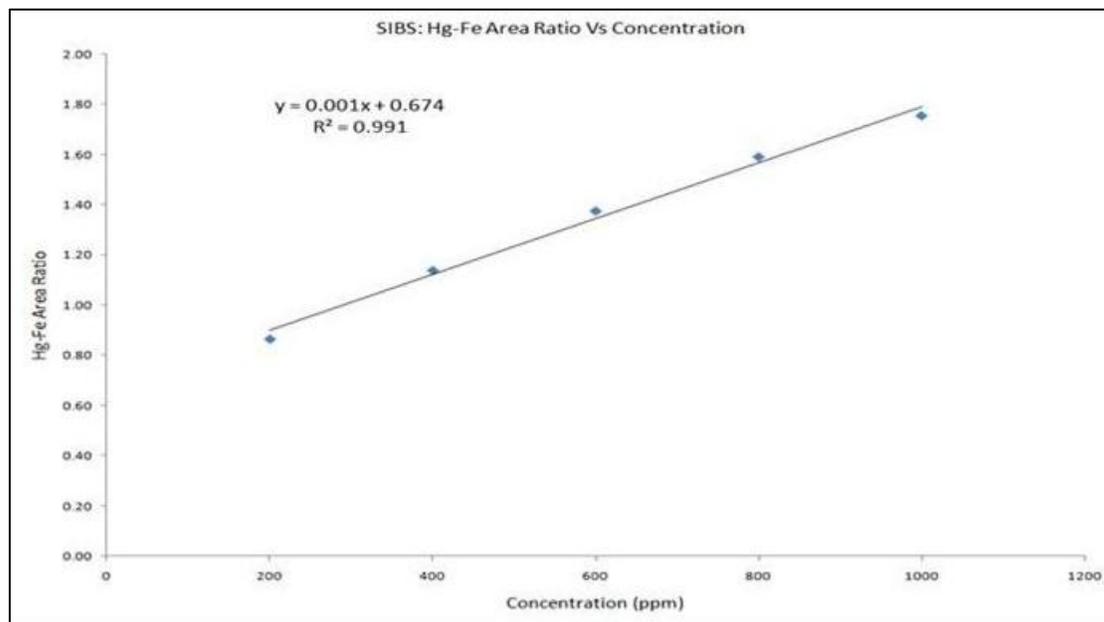


Figure 4.4 SIBS calibration with Hg-to-Fe peak area ratio

4.3 LIBS Calibration

Five standard soil samples (in pellet form) containing 500 ppm, 1000 ppm, 2500 ppm, 5000 ppm, 10000 ppm of mercury (Hg) as HgS were used for LIBS measurements. The acquired spectra were analyzed in the same way as in case of SIBS. The R^2 value for the calibration plot developed using the Hg intensity was found to be 0.997 but with a high RSD values. The relative standard deviation at the lowest concentration sample (500 ppm) was observed to be 31% while at higher concentrations the RSD values were observed to be below 9%. The limit of detection (LOD) using LIBS for mercury in soils was calculated to be 483 ppm. The calibration models developed using LIBS technique is as shown in Figures 4.5 to 4.8.

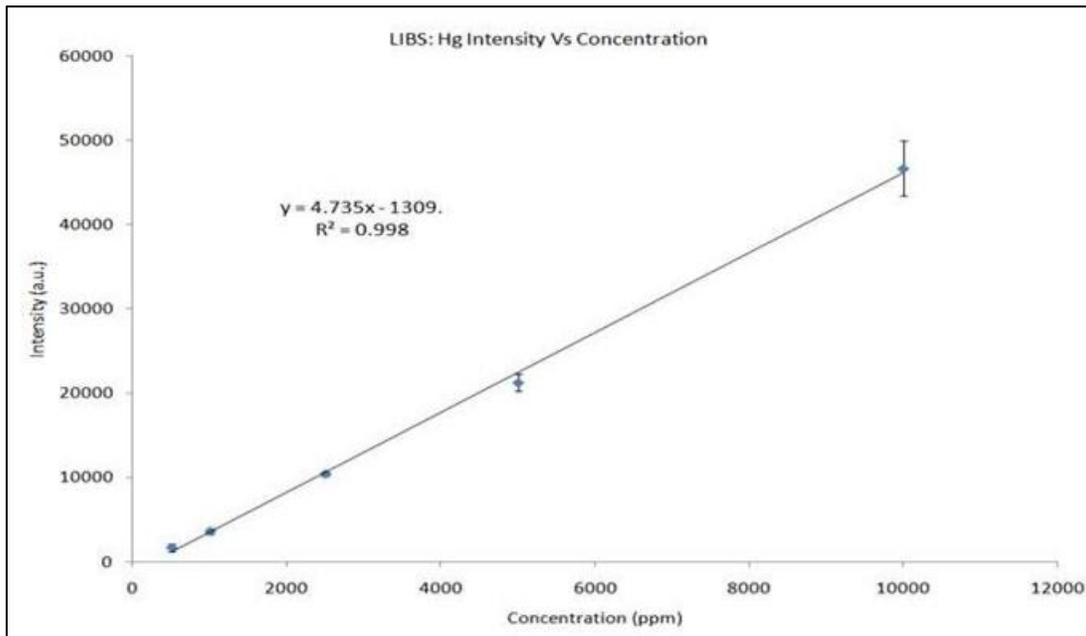


Figure 4.5 LIBS calibration with Hg intensity

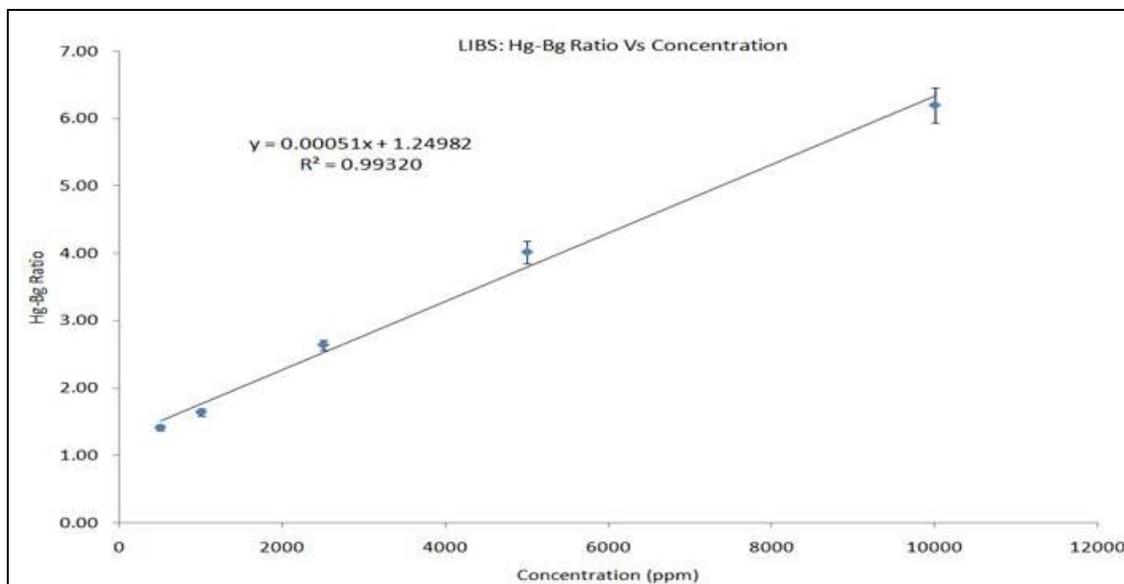


Figure 4.6 LIBS calibration with Hg-to-background ratio

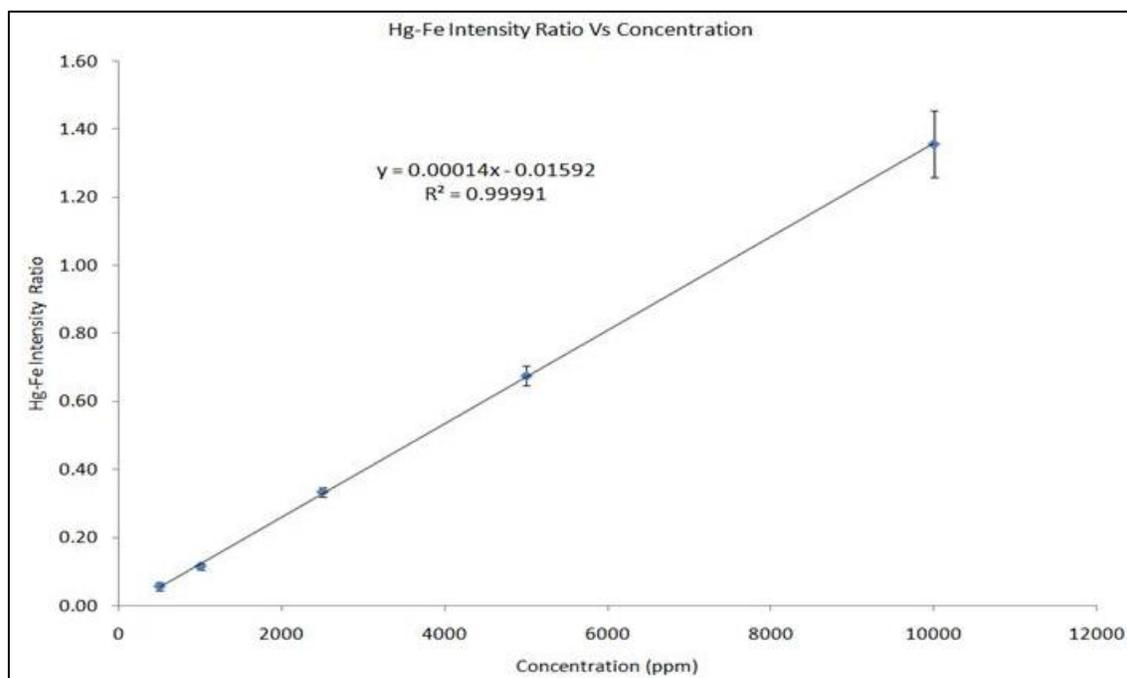


Figure 4.7 LIBS calibration with Hg-to-Fe intensity ratio

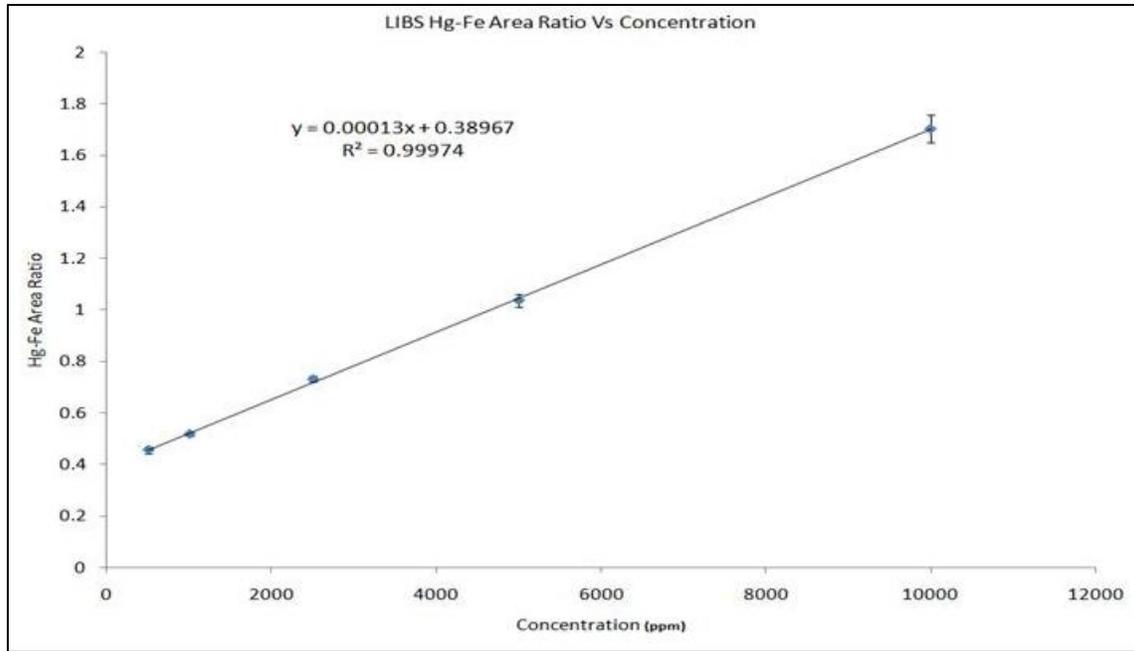


Figure 4.8 LIBS calibration with Hg-to-Fe peak area ratio

4.4 SIBS and LIBS Comparison

4.4.1 Types of Sample

The soil sample used for the LIBS measurements was in pellet form while for the SIBS measurements, the samples were in powder form. When pellets were used for SIBS measurements, the signal could not be detected, indicating that for pellets, higher energy was required for the breakdown and the energy from the spark was not sufficient for breakdown to generate a plasma. When a powder sample was used in LIBS measurements, poor signal was observed. The ejected sample (due to laser shots) resulted in the breakdown before the focal point to which the pickup lens was adjusted to receive signal. Also the pickup lens became contaminated due to the ejected sample. The reasons mentioned above might be responsible for poor LIBS signal for powder samples. The

calibration developed for Hg using the LIBS technique using samples in pellet form was in the region of higher concentration (in the range of 500 ppm – 10000 ppm). Using the present experimental setup and analysis technique, the limit of detection was observed to be 483 ppm which is very close to the least concentration sample used for calibration (500 ppm). Thus LIBS in the region of lower concentration (from 200 ppm to 1000 ppm) was not studied. The study was more focused on comparing the techniques in the regions of lower concentration of mercury (Hg) in soils. The calibration in higher concentration region was not developed for the SIBS technique though it would make the study more robust. Thus we used pellets samples of higher concentration (in the range of 500 ppm to 10000 ppm) for LIBS measurements and powder samples of lower concentration (in the range of 200 ppm to 1000 ppm) for SIBS measurements.

4.4.2 Spectra and Calibration

The standard deviations from LIBS measurements were observed to be smaller than those of SIBS. This could be observed by comparing the spectra of LIBS and SIBS at same concentration. The variation in background was observed to be significant in SIBS spectra while the background remained almost constant in LIBS spectra. This implies that there existed a larger plasma variation in the spark-induced plasma compared to the variation in the laser-induced plasma. The presence of the soil sample in the region of spark, the variation in distance of separation between the electrodes due to the spark itself might be affecting the plasma generated. To minimize the effects of this variation in calibration, ratiometric method was applied. The ratio of mercury analyte line to the background near the analyte line was considered for developing the calibration model. Thus the calibration with Hg-Intensity is more accurate and linear in LIBS while Hg-to-

background ratio gave a good linear calibration for SIBS. The comparison of the LIBS and SIBS spectra are as shown in Figure 4.9.

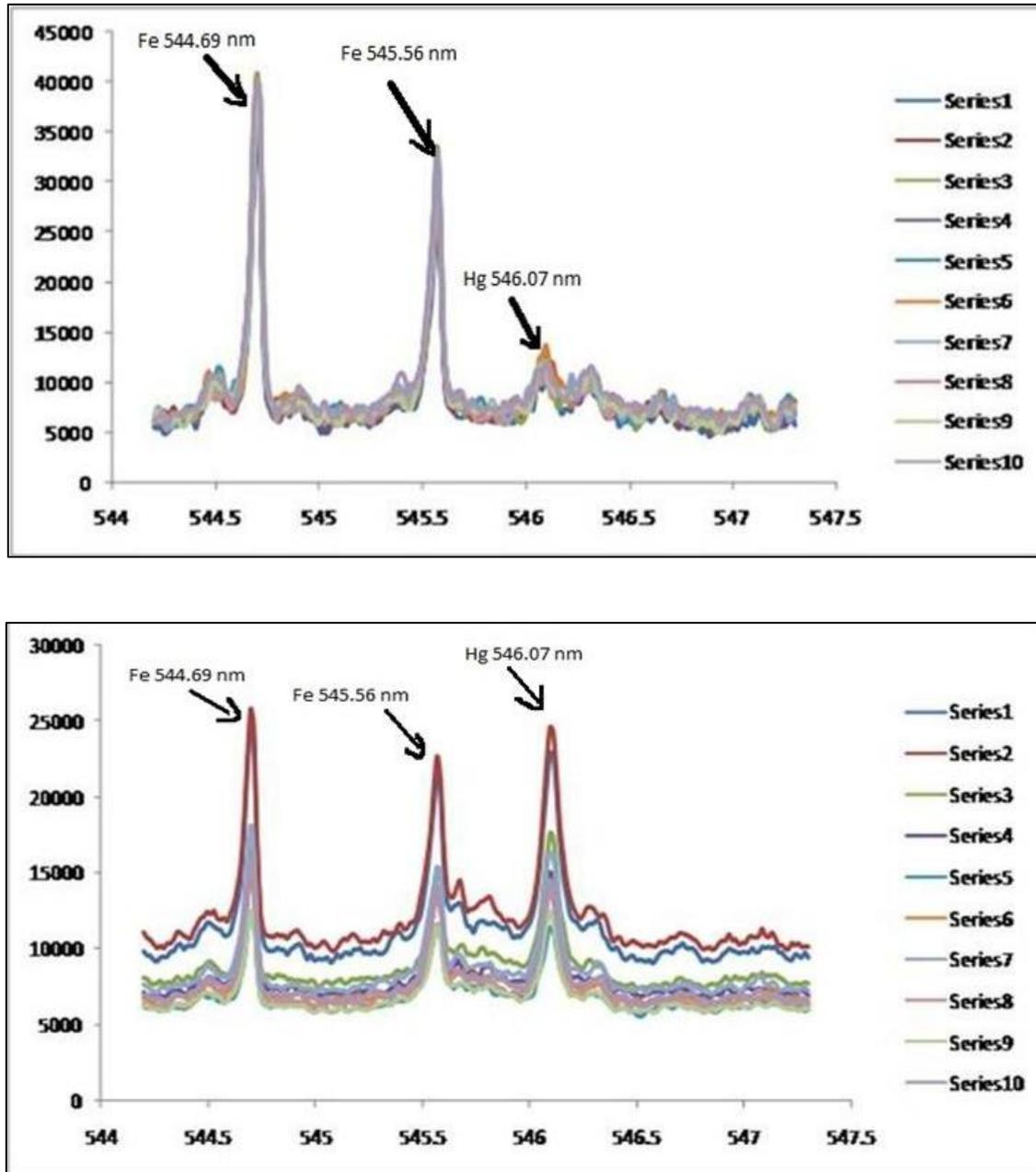


Figure 4.9 LIBS spectra (above) and SIBS spectra (below)

4.4.3 Limit of Detection

The limit of detection was calculated using the IUPAC definition of $LOD = 3\sigma/m$ where m is the slope obtained from the calibration plot and σ is the standard deviation of the background. It was observed that the limit of detection using SIBS technique was 20 ppm and for that of LIBS is 483 ppm by considering univariate analysis of the Hg 546.07-nm analyte line. The LIBS calibration was observed to be better for high concentration samples while at lower concentration, SIBS calibration is beneficial. The parameters utilized in this study can be summarized as follows:

Table 4.1 Summary of LIBS and SIBS operational parameters

	Sample Type	Experimental Conditions	Limit of detection	Remarks
SIBS	Powder sample	High Voltage: 1kV Gate Delay: 40 μ s Gate Width: 50 μ s Exposure time: 0.5s MCP voltage: 600v Spark frequency: 2.5Hz	20ppm	Samples used for calibration were in the region of lower concentration (in the range of 200ppm to 1000ppm)
LIBS	Pellet sample	Laser Energy: 62.5mJ/Pulse Gate Delay: 1 μ s Gate Width: 5 μ s Exposure time: 1s MCP voltage: 800v Laser frequency: 5Hz	483ppm	Samples used for calibration were in the region of higher concentration (in the range of 500ppm to 10000ppm)

CHAPTER V

CONCLUSION AND FUTURE DIRECTIONS

Spark Induced Breakdown Spectroscopy and Laser Induced Breakdown Spectroscopy are atomic emission based techniques that use high energy excitation sources. Both these techniques have some advantages over the traditional atomic emission techniques in terms of sample preparation, *in situ*, rapid and real time analysis. The present work is a basically a study of these two potential techniques for quantification of mercury (Hg) in soils. The method of data analysis used for this study is the univariate approach i.e. using a single analyte line for analysis. Though these techniques have advantages, they are susceptible to variations in environment and in experimental parameters making the reproducibility of plasma a difficult task. LIBS and SIBS are pulsed discharges whose plasma parameters (i.e., plasma temperature, electron density, plasma volume, etc.) vary with the time. It has been observed that the parameters affecting the plasma are energy of the excitation source, gate delay and gate width. It has also been observed that choice of the analyte line is important as it should be free from interference effects. The analyte line chosen for the analysis is the 546.07-nm mercury line. Then the optimum conditions for these experimental parameters were determined and using these parameters, the calibration models for SIBS and LIBS were developed. When LIBS spectra were compared to the spectra of SIBS, it was observed that the plasma condition (background) was almost constant in LIBS spectra while

background in SIBS varied. Thus the calibration developed using the Hg-to-background ratio was more linear compared to calibration developed using Hg intensity for SIBS while for LIBS Hg intensity calibration was observed to be more linear.

From the present study it could be concluded that SIBS is more efficient with powder samples in a low concentration region for quantification of mercury in soils while LIBS is efficient in the region of higher concentrations using pellet samples. The study could be further extended by applying more robust sampling and data analysis techniques (such as advanced chemometric techniques) to investigate for the improvement in the sensitivity of Hg detection. As mentioned earlier, the emission characteristics vary with gaseous atmosphere surrounding the sample, the effect of purging with argon can be investigated for both LIBS and SIBS. The SIBS sampling system needs to be modified accordingly in order to allow for gas purging. Also it can be investigated if laser assisted SIBS would be more efficient in both higher and lower concentration regions for quantification of mercury in soils.

REFERENCES

- [1] Fengxiang X. Han, Amos Banin, Yi Su, David L. Monts, M. John Plodinec, William L. Kingery, and Glover E. Triplett, "Industrial Age Anthropogenic Inputs of Heavy Metals into the Pedosphere," *Naturwissenschaften* 89, 497-504 (2002).
- [2] Fengxiang X. Han, Yi Su, David L. Monts, M. John Plodinec, Amos Banin, and Glover E. Triplett, "Assessment of Global Industrial-Age Anthropogenic Arsenic Contamination," *Naturwissenschaften* 90, 395-401 (2003).
- [3] Nicolas H. Bings, Annemie Bogaerts, and Jose´ A. C. Broekaert, "Atomic Spectroscopy: A Review," *Anal. Chem.* 82, 4653–4681 (2010).
- [4] Gauglitz, G. and Vo-Dinh, T. *Handbook of Spectroscopy* (Wiley-VCH, 2003).
- [5] Beckhoff, B., Kanngießer, B., Langhoff, N., Wedell, R., Wolff, H., *Handbook of Practical X-Ray Fluorescence Analysis* (Springer, 2006).
- [6] R. Gaudio, M. Dell'Aglio, O. De Pascale, G. S. Senesi, and A. De Giacomo, "Laser Induced Breakdown Spectroscopy for Elemental Analysis in Environmental, Cultural Heritage and Space Applications: A Review of Methods and Results" *Sensors* 10(8), 7434-7468 (2010).
- [7] A. Argyraki, M. H. Ramsey, and P. J. Potts, "Evaluation of Portable X-ray Fluorescence Instrumentation for in situ Measurements of Lead on Contaminated Land" *Analyst* (Cambridge, U.K) 122, 743-749 (1997).
- [8] A. Miziolek, V. Palleschi, and I. Schechter, *Laser-Induced Breakdown Spectroscopy (LIBS): Fundamentals and Applications* (Cambridge U. Press, 2006).
- [9] J. P. Singh and S. N. Thakur, *Laser-Induced Breakdown Spectroscopy* (Elsevier, 2007).
- [10] D. Cremers and L. J. Radziemski, *Handbook of Laser-Induced Breakdown Spectroscopy* (Wiley, 2007).
- [11] A. J. R. Hunter, S. J. Davis, L. G. Piper, K. W. Holtzclaw, M. E. Fraser, "Spark-Induced Breakdown Spectroscopy: A New Technique for Monitoring Heavy Metals," *Appl. Spectrosc.* 54, 575-582 (2000).

- [12] Amy J. R. Hunter, Richard T. Wainner, Lawrence G. Piper, and Steven J. Davis, "Rapid field screening of soils for heavy metals with spark-induced breakdown spectroscopy." *Appl. Opt.* 42, 2102-2109 (2003).
- [13] Morgan S. Schmidt and Amy J. Ray Bauer, "Preliminary correlations of feature strength in spark-induced breakdown spectroscopy of bioaerosols with concentrations measured in laboratory analyses," *Appl. Opt.* 49, C101-C109 (2010).
- [14] N. Kawahara, E. Tomita, S. Takemoto, Y. Ikeda, "Fuel concentration measurement of premixed mixture using spark-induced breakdown spectroscopy," *Spectrochimica Acta Part B* 64, 1085-1092 (2009).
- [15] G. S. Senesi, R. Gaudiuso, M. Dell'Aglio, O. De Pascale, C. Zaccone, M. Capitelli, and A. De Giacomo, "Heavy metal concentrations in soils as determined by laser-induced breakdown spectroscopy (LIBS), with special emphasis on chromium" *Environmental Research* vol 109, Issue 4, 413-420 (2009).
- [16] T. Hussain, M. A. Gondal, "Monitoring and assessment of toxic metals in Gulf War oil spill contaminated soil using laser-induced breakdown spectroscopy" *Environmental Monitoring and Assessment*, vol 136, Issue 1-3, 391-399 (2008).
- [17] Michael E. Essington, Galina V. Melnichenko, Melanie A. Stewart, and Robert A. Hull, "Soil Metal Analysis Using Laser-Induced Breakdown Spectroscopy (LIBS)" *SSSAJ*, vol 73, 1469-1478 (2009).
- [18] Amina Ismael, Bruno Bousquet, Karine Michel-Le Pierres, Gregorie Travaille, Lionel Canioni, and Stephane Roy, "In situ Semi-Quantitative Analysis of Polluted Soils by Laser-Induced Breakdown Spectroscopy (LIBS)" *Applied Spectroscopy*, vol 65, 467-473 (2011).
- [19] J. P. Walters, "Historical advances in spark emission spectroscopy" *Applied Spectroscopy*, vol 23(4), 317-331 (1969)
- [20] L. Paksy, B. Nemet, A. Legyel, L. Kozma and J. Czevkel, "Production control of metal alloys by laser spectroscopy of molten metal" *Spectrochim. Acta Part B* 51, 279-290 (1996).
- [21] F. Y. Yueh, J. P. Singh, and H. Zhang, "Laser-induced breakdown spectroscopy elemental analysis" in *Encyclopedia of Analytical Chemistry*, R. A. Meyers, ed. pp. 2066-2087 (Wiley, New York, 2000).
- [22] Amy J. R. Hunter and Lawrence G. Piper "Spark-induced breakdown spectroscopy: a description of an electrically generated LIBS-like process for elemental analysis of airborne particulates and solid samples" in *Laser Induced Breakdown Spectroscopy-Fundamentals and Applications*, (Cambridge U. Press 2006).

- [23] S. Rosenwasser, G. Asimellis, B. Bromley, R. Hazlett, J. Martin, T. Pearce, and A. Zigler, "Development of a method for automated quantitative analysis of ores using LIBS," *Spectrochim. Acta Part B* 56, 707–714 (2001).
- [24] M. Martin, S. Wullschleger and C. Garten Jr, "Laser-induced breakdown spectroscopy for environmental monitoring of soil carbon and nitrogen," *Proceedings of SPIE*, Eds. Tuan Vo-Dinh and Stephanus Buttgenbach, vol 4576, pp. 188-195 (2002).
- [25] R. Krasniker, V. Bulatov and I. Schechter, "Study of matrix effects in laser plasma spectroscopy by shock wave propagation", *Spectrochim Acta B*56, 609-618 (2001).
- [26] NIST Atomic Spectra Database Lines Data <http://www.nist.gov/pml/data/asd.cfm>
- [27] C. Lazzari, M. De Rosa, S. Rastelli, A. Ciucci, V. Palleschi and A. Salvetti, "Detection of mercury in air by time-resolved laser-induced breakdown spectroscopy technique," *Laser and Particle Beams* 12: 525-530 (1994)
- [28] Walid Tawfik, Ali Saafan, "Quantitative Analysis of Mercury In Silver Dental Amalgam Alloy Using Laser Induced Breakdown Spectroscopy With a Portable Echelle Spectrometer," *International Journal of Pure and Applied Physics* 3, 195-203 (2006).
- [29] R L Gleason, D W Hahn, "The effects of oxygen on the detection of mercury using laser-induced breakdown spectroscopy," *Spectrochimica Acta Part B: Atomic Spectroscopy* 56 (4), 419-430 (2001).
- [30] Meng-Dawn Cheng, "Real-time measurement of trace metals on fine particles by laser-induced plasma techniques," *Fuel Processing Technology* 65–66 (2000) 219–229.
- [31] Barbini, R., F. Colao, R. Fantoni, A. Palucci and F. Capitelli "Application of laser-induced breakdown spectroscopy to the analysis of metals in soils". *Applied Physics A*, 69 (1999) 175-178.
- [32] Xu, L., V. Bulatov and V.V. Gridin " Absolute Analysis of Particulate Materials by Laser-Induced Breakdown Spectroscopy" *Analytical Chemistry*, 69 (11) (1997) 2103-2108.
- [33] Kaiser, J., O. Samek, L. Reale, M. Liška, R. Malina, A. Ritucci, A. Poma, A. Tucci, F. Flora, A. Lai, L. Mancini, G. Tromba, F. Zanini, A. Faenov, T. Pikuz and G. Cinque "Monitoring of the heavy-metal hyper accumulation in vegetal tissues by X-ray radiography and by femto-second laser induced breakdown spectroscopy" *Microscopy Research and Technique* 70 (2007) 147-153.

APPENDIX A
CIRCUIT SCHEMATIC OF TRIGGERING SYSTEM AND HIGH VOLTAGE
SYSTEM

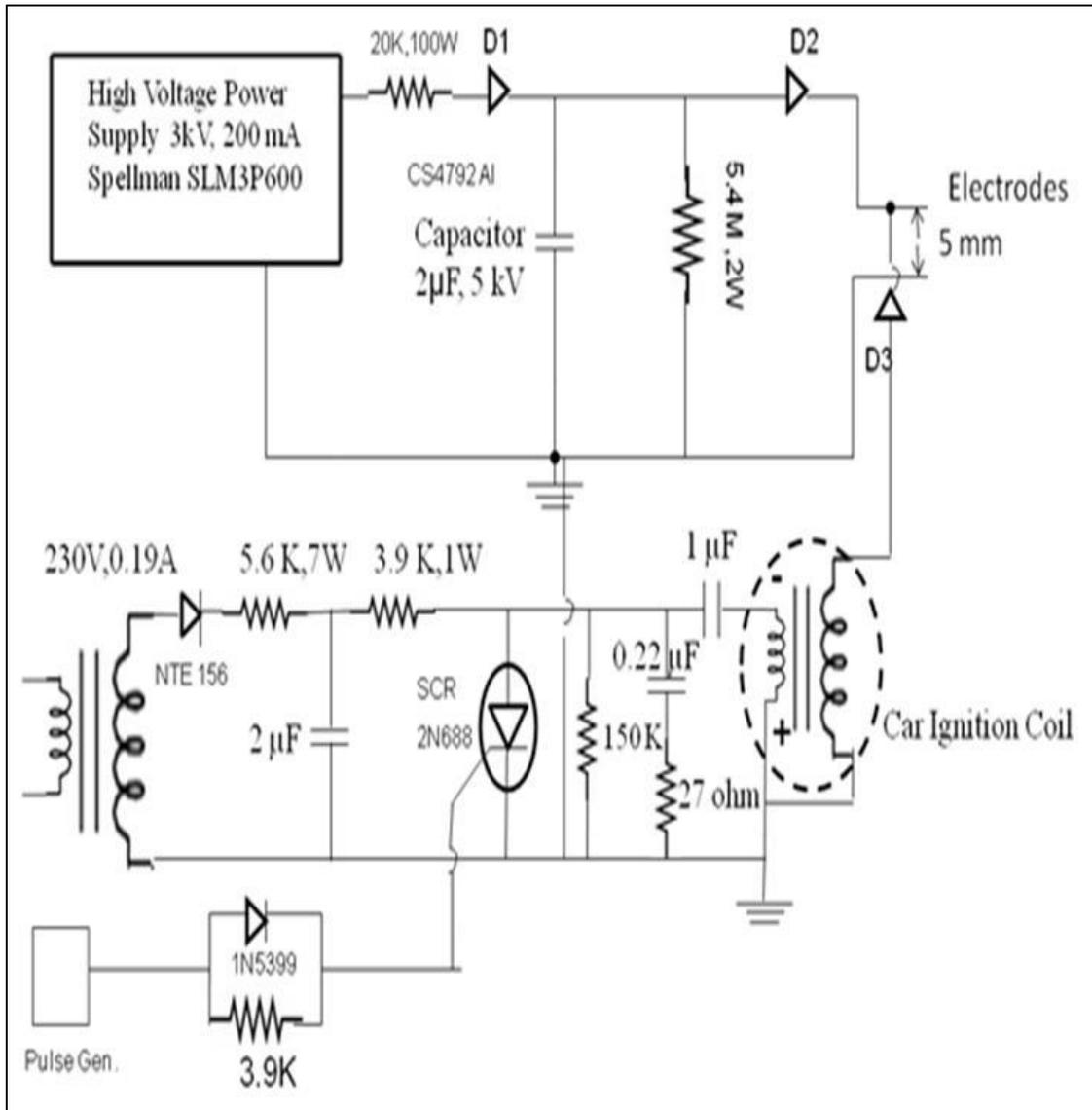


Figure A.1 Circuit schematic of triggering system and high voltage system