## LASER INDUCED BREAKDOWN SPECTROSCOPY UTILISING SYNTHETIC SPECTRUM METHOD FOR OPTICALLY THICK PLASMAS

A thesis submitted in partial fulfilment of the requirements for the degree of

of

**Doctor of Philosophy** 

by

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under the supervision of

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## DEPARTMENT OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY GANDHINAGAR

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This is to certify that this thesis entitled Laser Induced Breakdown Spectroscopy Utilising Synthetic Spectrum Method for Optically Thick Plasmas submitted by Mr. Prashant Kumar (Roll No. 15330021), to the Indian Institute of Technology Gandhinagar, is a record of bona fide research work carried out under my supervision and has not been submitted elsewhere for the degree. I have read this dissertation and in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

> **Prof. Ravindra Pratap Singh** Senior Professor Atomic, Molecular and Optical Physics Division Physical Research Laboratory, Ahmedabad (Thesis Supervisor)

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## Abstract

Laser induced breakdown spectroscopy (LIBS) has emerged as one of the promising analytical technique for quantitative analysis. This method offers several advantages in terms of versatility and ease of setting up the experiment when compared with other analytical methods. Although there has been a substantial understanding of most of the basic processes involved in LIBS such as laser-matter interactions, plasma formation, its propagation and temporal evolution, etc, still a significant amount of research into utilising the emission spectrum from an evolving plasma to obtain accurate quantitative information is required. This has been a driving force for nearly two decades of active research in the field.

The present thesis is also aimed towards achieving the goal of obtaining more reliable and accurate results using LIBS for materials with varying degree of complexity in terms of analysis. Considering the advantage that no additional information or data of the analyte, apart from the emission spectra, is needed, the present thesis is based on an approach known as calibration-free LIBS. The work presented in the thesis is mainly focused on synthetic spectrum method for quantitative analysis. This method is based on comparing the experimental spectrum with a simulated LTE spectrum of the material under study where all plasma parameters including number densities of species and hence, concentration is obtained as a result of simultaneous fitting of multiple emission lines in a spectrum. Improvements to the technique have been realized by using a large number of emission lines in the analysis and an automated search procedure for line identification. The effectiveness and suitability of the developed method has been demonstrated on different samples, even for cases having dense spectrum with merged lines. The method has also been used for estimating detection limits for various trace elements in the sample as a function of experimental signal-to-background levels. This can help in deciding the experimental conditions tuned to analyze selected trace elements. A correct accounting of the emission line broadening, mainly due to self-absorption and Stark effect in the plasma is of utmost importance in matching the experimental spectrum with simulated one. Although the developed scheme of analysis automatically incorporates the effect of self-absorption in the plasma, much accurate estimate of Stark broadening still poses a challenge given the paucity of available data in literature. A correct estimate of this parameter becomes even more important as self-absorption in turn depends on Stark broadening of the emission line. Hence, a method utilising time resolved measurements have been proposed for Stark broadening measurements. This utilises the relation between various emission line parameters and the plasma opacity. The method has been successfully demonstrated on a few resonant lines of neutral aluminum species. With these improvements, major objectives of the present thesis have been realized. The suggested procedure also paves a way to further research in some of the topics, such as obtaining temporal evolution of the detection limits for different elements, estimating error expected in quantitative analysis in CF-LIBS using synthetic spectrum method, Stark parameter database for LIBS, etc.

# **List of Publications**

## Publications in refeered journal/book chapter related to present thesis

- "Determination of Stark Shifts and Widths Using Time-Resolved LIBS Measurements", Prashant Kumar, Swetapuspa Soumyashree, Nageswara Rao Epuru, Swaroop B Banerjee, R P Singh and K P Subramanian, Applied Spectroscopy, 2020 (accepted)
- "Optical Signal Enhancement in LIBS Using Aluminum Nanoparticles on Brass Sample", E. Nageswara Rao, Swetapuspa Soumyashree, Prashant Kumar, Pooja Chandravanshi, Swaroop Banerjee, K. P. Subramanian, Rajesh K. Kushawaha, Advances in Spectroscopy: Molecules to Materials, Springer, Singapore, 2019
- "Quantitative estimation of elemental composition employing a synthetic generated spectrum", Prashant Kumar, Rajesh K Kushawaha, S B Banerjee, K P Subramanian, and N G Rudraswami, Applied Optics 57, No. 19, 2018, 5443

#### To be submitted

 "Detection limits in quantitative analysis of rock sample using synthetic spectrum method for LIBS"

# Acronyms

LIBS	Laser Induced Breakdown Spectroscopy
CF-LIBS	Calibration Free - Laser Induced Breakdown Spectroscopy
IB	Inverse Bremsstrahlung
LTE	Local Thermodynamic Equilibrium
ICCD	Intensified Charge Couple Device
EPMA	Electron Probe Micro-Analyser
XRF	X-Ray Fluorescence
SBR	Signal-to-Background Ratio

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## Chapter 1

## Introduction

## **1.1** Development of a new analytical method

Emission spectroscopy, as is true for any other branch of physics, has a very long and interesting heritage. With passing of generations, emergence of new methods combined together with the pioneering work by scientists of that era, has shaped the course of this particular field. This modern-day analytical technique, called as optical emission spectroscopy (OES), has its lineage from the lecture delivered by Thomas Melvill in 1752 to the Medical Society of Edinburgh [1]. This lecture entitled, "Observations on light and colors", presented the results of probably the first flame test conducted on salts describing the observance of enhancement in yellow light when viewed with a prism. This was followed by Andreas Sigismund Marggraf observation on color of light emitted by different element rich compounds. This clearly distinguished between potassium and sodium rich compounds through distinctive flame color [2]. These observations along with a couple of more observations on element specific flame color were made in the later half of the 18th and early 19th century [2].

A more systematic and serious spectroscopic investigation had to wait until 1860s when Robert Bunsen and Gustav Kirchhoff finally develop the first spectroscope. This consisted of lens and slit assembly for light collection, prism mounted on a turntable for light dispersion and telescopic arrangement with filters for observation [2, 3]. The use of narrow slit before dispersing element to limit in the light, although, was demonstrated earlier by W H Wollaston in 1802 and Joseph Fraunhofer in 1814 who were successful in observing the line spectrum [4]. The development of the spectroscope soon led to the discovery of two elements, cesium and rubidium [3] and many other elements in the late 19th and early 20th century [5].

The emission spectroscopy, till this time, was mainly focused on more of a "qualitative" use for identification of elements and complex "quantitative" analysis started only when its use for geo-chemical samples started in late 1920s [5]. This transition from the qualitative to accurate quantitative analysis of various samples compels one to have a much more stable emission sources and sensitive detectors. The success of emission spectroscopy as analytical technique has been majorly driven by the technological advancement during second half of the last century. Starting from inductively coupled plasma(ICP) to spark/glow discharge and then laser ablation have proved to be remarkable methods for emission sources used for a variety of targets. Among the various existing emission sources employed in OES, the laser ablation(LA) method has been most promising in recent times. This is primarily because of two reasons, first being the variety of samples containing different elements which can be probed using LA method when compared with the limited targets that can be employed in other methods (ICP or spark discharge). The second and the most distinctive advantage LA method provide is the fact that the plasma can be generated remotely which opens up a possibility to utilize this method for a range of scenario. The LA method for generating plasma emission source combined with the OES technique has been traditionally termed as laser induced breakdown spectroscopy (LIBS) and is the central theme on which the present thesis is based.

LIBS has revolutionized the field of material analysis since its inception in early 1980s [6-8]. The term 'breakdown' in LIBS draws its analogy with the electrical breakdown in gases under extreme electric fields [9]. Similar ability of high power lasers to vaporize, ionize and excite the plasma resulted in a huge impetus to the development of quantitative elemental analysis by studying the plasma emission spectrum. With the advancement in the technology of lasers and ultra-fast detectors, what originally was conceived only for qualitative detection of elements can now provide accurate quantitative results for material composition comparable with other established conventional methods [7, 9-12]. The ver-

satility of LIBS technique is not only because of its applicability to various analyte but also due to different ambient conditions where it can be employed [12–18]. This compounded with negligible sample preparation makes it an ideal candidate for various remote sensing and planetary exploration applications as well [12, 19–22].

The route to determination of elemental concentrations from the captured plasma emissions utilises basic physics of the transient laser produced plasma. Irrespective of temporal characteristics of the excitation source or the ambient, the plasma evolution is marked by a characteristic change in its spectral properties which is mainly governed by the change in two plasma parameters, namely, number density of species and temperature [7, 9]. As the plume evolves, there is an overall fall in these parameters and the plasma emission which starts with a huge continuum, rapidly changes to characteristic line emissions and gradually fades down [7, 9, 23]. Figure 1.1 shows the general behavior of the emission from such transient plasma. The timescale and source of these changes in the emission properties are mainly governed by the excitation laser pulse width and the ambient. Although a much more detailed discussion on these aspects will be presented later in this chapter, it is important to note from figure 1.1 that to record characteristic line emissions for elemental analysis, the plasma signal has to be recorded in a particular time window.

The accuracy of result of the quantitative analysis is dependent on the interplay of choice of the time window and corresponding signal-to-background ratio of the recorded spectrum [24]. Once a proper time window for acquisition is established, the analysis of the emission line profiles to retrieve elemental composition follows two different approaches. The first approach relies on a calibration curve drawn using relative line intensities for various concentrations of minor element to a major element in the sample. The method has been traditionally called as "Calibration-based" LIBS and has been quite successful for laboratory analysis of standard samples of known sample constituents [7, 11, 12]. But, it has to overcome three major challenges which makes it difficult to be used for many samples and applications. The first one is the dependence of the spectral signals from the minor element of the analyte on the overall material composition. Hence, a calibration curve obtained for a minor element depends on the concentration of the major element in which it is prepared (the matrix). This issue is well known as the "matrix effect" in



Figure 1.1: Temporal changes in the emission characteristics of the plasma generated using nano-second laser ablation in air. The resulting spectrum is also shown at different time delay (marked with arrow) for Aluminum plasma. Note the presence of huge continuum during early acquisition time and clean line spectrum after certain acquisition delay.

LIBS [7, 25]. The second disadvantage is the tedious process of preparation of sample with varied composition for making calibration curve. The other major disadvantage is the non-linearity of the calibration curves for major elements due to self absorption in the emission lines which limits the accuracy of concentration determination [23].

To overcome these issues, Ciucci et al. [26] proposed a new method, known as "Calibration-Free" LIBS which relies only on the spectral signatures from the plasma to perform a quantitative analysis. It utilises the radiative transfer equations to relate line intensities to the number density of various species from which the concentration is calculated [27, 28]. The present thesis is based on this method where two different approaches for elemental analysis will be presented for optically thin and thick plasma conditions. To employ the number density relation with observed line emission intensity, certain approximations and assumptions are necessary. The prominent among those assumptions is the assumption of local thermodynamic equilibrium for the emitting species during acquisition time window. This makes CF-LIBS procedure sensitive to the experimental conditions used for recording the spectrum. This along with other assumptions such as plasma homogeneity and stoichiometric ablation will be discussed later.

The layout of the present chapter is as follows. First a brief account of plasma formation and its dependence on the laser parameters will be presented. The discussions will be limited only to the nanosecond time scale of excitation sources. This will be followed by discussions on temporal evolution of plasma number density, temperature and spectral characteristics. A review of various assumptions in the context of the use of the optical signatures for quantitative elemental analysis using CF-LIBS will be presented next. At last, motivation of the present thesis work along with an overview will be presented.

## **1.2** Plasma formation

The interaction of laser pulses with gases resulting in fast ionization and plasma formation has been reported as early as 1960s [29]. Such non-linear absorption of photons resulting in ionization using photon energies much lower than the ionization potential resulted in theories different from the conventional processes of electron impact or photoionisations. Two prominent processes were then identified which can drive these ionizations, namely, multiphoton ionization and inverse bremsstrahlung (IB) followed by electron impact ionization [9, 30].

Multi-photon ionization is the process wherein multiple photons of energy  $\hbar\omega$  from an intense laser source are absorbed by a single bound electron of ionization energy,  $E_{ion}$ , such that,  $n\hbar\omega \ge E_{ion}$ . The probability of this photon absorption is roughly proportional to the 2*n*-th power of laser electric field [30]. Cascade ionization or electron avalanche results from free electrons gaining energy in the photon field in presence of other charged ions through IB process. Once the electron gains sufficient energy, it results in ionization creating more electrons to start the process all over again. The newly generated electrons further multiply the process resulting in an avalanche [9, 30]. The above discussion related to plasma formation in gases can be extended to solids with the additional steps of heating, melting and vaporization. The plasma formation in this case is delayed because of these additional steps. The interaction of nanosecond laser pulse resulting in melting and subsequent formation of plasma can be a result of thermal or non-thermal process or a combination of both depending on the laser irradiance. Typically for laser irradiance  $< 10^8$  W/cm<sup>2</sup>, the prominent process is thermal whereby the energy coupling between the solid target with the laser light is a result of transforming electronic excitation of the lattice into heat through phonon vibrations [30]. Typically, the timescale for phonon relaxation is of the order of few picoseconds and hence results in efficient heating of the target within the laser pulse duration. For higher power densities, non-thermal coulomb explosion also contributes towards material ablation. In this case, high power results in removal of valence electrons and generation of high energy electrons and ions through avalanche ionization which weakens the lattice and results in explosion of the surface. This process also ensures that the stoichiometry of the ablated particle and hence the resultant plasma remains same as of the target material [23].

In context of these processes resulting in plasma formation, a brief discussion on the dependence of the above processes on some of the laser parameters is presented. The discussions will be mainly focused on the physical processes resulting from the use of nano-second pulses.

## **1.3** Laser parameter dependence

Laser sources used to create plasma have evolved vastly since the invention of first laser source [31, 32]. A host of intense, monochromatic and spatio-temporal coherent sources are now readily available for LIBS. With pulsed lasers of a few nanoseconds to femtoseconds, one can easily achieve intensities of the order of  $10^9 - 10^{12}$  W/cm<sup>2</sup>. The advantage to deliver high radiance is presumably an important parameter when compared with the monochromaticity or coherency of these sources [30]. For typical LIBS application, important characteristic of the laser to be considered is laser wavelength extending from UV to IR and its pulse duration. Quality factor( $M^2$ ) of the laser defining its spatial energy distribution is also a factor for LIBS as the produced plasma and its propagation and resulting radiation depends on the ablation geometry [30].

Some of the above parameters in context to the present study will be presented in the subsequent sections. Moreover, since the results presented in this thesis involve solid samples, discussions related to laser interaction with solids only will be presented.

#### **1.3.1** Fluence, ablation efficiency and thresholds

Laser fluence is defined as energy per pulse falling onto per unit area  $(cm^2)$  of the target and has a unit of Joules/cm<sup>2</sup>. This is an important parameter as the ablation process starts when its value exceeds a threshold value. This is known as 'ablation threshold', typical value of which for metals is ~ 1 Joules/cm<sup>2</sup> [33, 34]. This value of fluence is easily achievable with present laser systems. For example a typical Q-switched nano-second Nd:YAG laser operating at its fundamental wavelength can deliver energies of few mJ to hundreds of mJ per pulse which can be focused to sub millimeter spot size resulting in fluence well above this threshold. A brief discussion on this will be presented in the next chapter when the experimental system used for the present study is discussed.

#### 1.3.2 Wavelength

The coupling of laser energy with the target in the ablation process is dependent on laser wavelength; UV sources showing relatively more energy absorption when compared with the IR lasers [23, 30]. Combined with the fact that UV lasers can be focused to a tighter spot, this results in an enhanced ablation efficiency.

As discussed in the previous section, the two processes responsible for plasma formation and excitation, namely electron collision -inverse bremsstrahlung (IB) and multiphoton ionization are dependent on the laser wavelength to a great extent. The process of collisional excitation - IB results in a  $\lambda^3$  dependence on the ablation threshold [9]. As a result, it is a major process when excitation is through IR wavelengths. At UV wavelengths, the multi-photon ionization becomes dominant source for initial generation of the seed electrons [9, 30] while electron growth is still governed by the IB process. Remaining sections of the present chapter will deal with the general properties of the plasma formed after the ablation process.

#### **1.3.3** Laser pulse duration

An important factor governing the plasma formation is the pulse duration of the excitation laser. As discussed previously, for nano-second lasers, the initial heating and vaporization of the target occurs during first few nanoseconds while majority of the later part causes further heating and ionization. The thermal diffusion timescale in this case is less than the pulse duration and hence a considerable amount of heat propagates in the target resulting in damage to the material appearing in the form of craters. For comparison, with pico and femto-second pulses, the damage is minimal resulting in precise removal of material with higher ablation rates [9]. This can be seen from the SEM images of craters formed due to laser pulses of varying duration [35].

## **1.4 Plume evolution**

In case of the solid target, after the onset of plasma formation, the resulting shock-wave drives the plasma perpendicular to the target surface irrespective of the direction of the incident laser. Also there are some marked differences in the number density, temperature and spectral characteristics as the plume propagates away from the a target depending on the ambient medium. The present thesis is based on experiments conducted in vacuum as well as in air. Hence, a discussion on its propagation in these two mediums will be presented as it results in setting up of some of the relevant experimental parameters and plasma properties to be utilised in models used later in the analysis. Moreover, since this study is mainly related to spectroscopy of the evolving plasma, only bulk parameters of the plasma and its spectral characteristics will be discussed.

### **1.4.1** Number density and temperature characteristics of the plasma

Typically, plasma temperatures of 18,000-20,000K and electron number densities of the order of  $10^{20} cm^{-3}$  are reached after the the formation of the plasma using nanosecond laser ablation. Once it propagates in the ambient, the temperature drops and hence the degree of ionization in the plasma. The electron number density also falls off as it expands. The process of plasma expansion and its lifetime is different in different ambient. Plasma expanding into vacuum has comparatively smaller lifetime when compared with its expansion in air. In air, the lifetime is of the order of few tens of microseconds because of the confinement due to the ambient pressure. A lack of this confinement in vacuum leads to a plasma lifetime typically of the order of few hundreds of nanoseconds. The faster plume dynamics in this case results in number densities falling rapidly and hence acquisition time in this case has to start faster compared to the case of air. Another difference in the plume dynamics for the two cases is in the plume propagation. While for the case of vacuum, it is mostly represented by a 1-D model (with only axial dynamics; no radial components), the case with air as background requires 2D model for accurate description of plume propagation [30, 36].

### 1.4.2 Spectral characteristics of the plasma

The spectral characteristics of the plasma evolves in relation to the change in the number density and temperature of the plasma discussed above. An important difference in the evolution of spectral characteristics for vacuum and air is the time window for LTE and optical thickness of the plasma. As discussed previously, because of faster dynamics, LTE is reached sooner and is for a very short time for the case of vacuum. A faster drop in number densities in lack of confining medium leads to a comparatively thin plasma in this case. In comparison, self absorption effects are more prominent in case of spectral emission from plasma expanding in air [37].

Detailed discussion related to spectral emissions from plasma for different opacities will be presented later in chapters 3 and 4.

## 1.5 Assumptions in CF-LIBS procedure

### 1.5.1 Stoichiometric ablation

Stoichiometry defines the relative ratio of various elements present in the sample. For LIBS, at typical laser fluence mentioned previously, we assume that the plasma is stoichiometric, i.e., the plasma formed has the same composition as the target. Various experimental evidences suggest that the ablation process is stoichiometric and the material properties (thermal conductivity, roughness, ionisation energies, etc) do not significantly affect the relative abundances of the plasma constituents[38–40].

There are some reports discussing observation of varying elemental fractionation in multi-element samples having constitutents whose ionisation energies vary drastically [41, 42]. This effect of non-stoichiometric ablation is dominant when the value of laser fluence is very near to the ablation threshold [43]. For the present study, this effect has been ignored since the experiments were conducted at a fluence value much above the typical ablation thresholds for metals. This assumption is of great importance to LIBS, as it shifts all of the analysis to the plasma produced by way of ablation irrespective of the material properties of the target under study.

### 1.5.2 Plasma homogeneity

Because of the spatial distribution of the bulk plasma parameters, temperature and number density, the recorded spectral emission is expected to show a dependence on the geometry of the light collection. But under certain cases it can be safely considered to be homogeneous. For example, in case of plume propagation in an ambient, multiple reflections of the shock-wave produced by the back-scattered ejecta results in the homogenization of the plasma [44, 45]. This happens after a certain time delay and with the advantage of gated observations routinely used in LIBS, the acquisition time can be set so that a model for homogeneous plasma can be used to describe the obtained spectral emissions.

The results presented in this thesis assume homogeneous plasma for the recorded spectrum, but to complete the discussion, a brief account of the model to describe non-homogeneous plasma is presented in the following sub-section. This will be followed by an estimation of expected error due to assumption of homogeneous plasma.

#### 1.5.2.1 Multi-layer model for non-homogeneous plasma

This model assumes in-homogeneous layers for the plasma each defined by a unique value of temperature and number density. From numerous theoretical simulations and experimental observations it is well established that the central portion of plasma (plasma core) is comparatively hotter and have higher electron number densities when compared with the outer layers (peripheral zone) [46]. This is pictorially represented in figure 1.2.



Figure 1.2: A simplified two layer plasma model showing a hot plasma core and comparatively cooler periphery. The direction of light collection is marked with an arrow along with the length of the two zones.

Using radiative transfer equations, line emissions from plasma  $(I_{\lambda})$  with two layers having different values of plasma parameters can be constructed as follows,

$$I_{\lambda} = \frac{\varepsilon_{\lambda_2}}{\kappa_{\lambda_2}} \times \left(1 - \exp(-\kappa_{\lambda_2} l_2)\right) + \frac{\varepsilon_{\lambda_1}}{\kappa_{\lambda_1}} \times \left(1 - \exp(-\kappa_{\lambda_1} l_1)\right) \times \exp(-\kappa_{\lambda_2} l_2)$$
(1.1)

where,  $\varepsilon_{\lambda}$  and  $\kappa_{\lambda}$  correspond to the emission and absorption coefficient for the line respectively and *l* denotes the length of the plasma. The subscripts, 1 and 2 denote the parameters for core and periphery layer of the plasma. Hence, for n-layer plasma, the line intensity term will have *n* terms corresponding to *n* layers of different  $\varepsilon_{\lambda}$  and  $\kappa_{\lambda}$  in the above equation. The inherent dependence of temperature and electron number density on the above parameters will be clear in the coming chapters where these terms will be discussed in detail.

#### 1.5.2.2 Expected error due to assumption of homogeneous plasma

As mentioned previously, the analysis performed in this thesis assumes plasma to be homogeneous. Bredice et al. [47] have shown the effect of plasma in-homogeneity on the emission line profiles in a study performed to determine the Stark width parameters from the observed line profiles. The in-homogeneity is considered by using an, "in-homogeneity parameter" defined as ratio of length of homogeneous plasma core to to the total length of the plasma. Outside the homogeneous core, the plasma parameters namely the temperature and electron number density are allowed to fall linearly. By simulating spectrum with an initial condition for temperature and electron number density and a significantly small value of in-homogeneous case is very low. They estimated a typical change of  $\sim 3\%$  in line widths for the emission lines considered. Although, this study was conducted on specific set of emission lines with an assumed initial value of plasma parameters, the technique gives a rough indication of the expected accuracy in ignoring the plasma in-homogeneity.

## 1.5.3 Local thermodynamic equilibrium (LTE) assumption

One of the most important assumptions related to plasma made throughout this thesis is the assumption of local thermodynamic equilibrium (LTE). The condition implies that the whole system is characterized by a single temperature 'T' such that,

• Velocity follows Maxwell's distribution and

$$\frac{\mathrm{d}n(v)}{\mathrm{d}v} = 4\pi v^2 n(v) \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \times \exp\left(-\frac{mv^2}{k_B T}\right) \tag{1.2}$$

where n(v) gives the number of particles with velocity in the range of [v, v + dv] at a temperature, *T*.  $k_B$  is the Boltzmann constant and *m* is the mass of the particle.
#### 1.5. ASSUMPTIONS IN CF-LIBS PROCEDURE

• Population of electronic levels follows Boltzmann distribution,

$$n_j = \frac{ng_j}{U(T)} \times \exp(\frac{-E_j}{k_B T})$$
(1.3)

In the above equation,  $g_j$  represents the statistical weight of the upper energy level j and U(T) is the partition function.

• Ionization follows Saha's equation

$$\frac{n^{II}}{n^{I}}n_{e} = \left[\frac{(2\pi m_{e}k_{B})^{\frac{3}{2}}2}{h^{3}}\right]T^{\frac{3}{2}}\frac{U^{II}(T)}{U^{I}(T)} \times \exp\left(-\frac{\chi^{I}}{k_{B}T}\right)$$
(1.4)

where the superscripts *I* and *II* represent the value of parameters for neutrals and ions respectively and  $\chi^{I}$  is the ionization potential.

The LTE condition differs from total thermodynamic equilibrium as Planck law for radiation equilibrium is not satisfied for such plasma since it allows radiation to escape from the system. This effectively means that the radiation emitted from such plasma do not contribute much to the electronic energy level distribution and it is mainly collision dominant i.e., governed by electron collisions.

In context of the evolving LIBS plasma, it is important to obtain optimum acquisition time in the temporal evolution where the plasma can be described by the above LTE prescription. This is discussed in the next section where a discussion on the criterion for plasma to be LTE is presented.

#### 1.5.3.1 McWhirter criterion

For LIBS plasma to be in LTE, the dominance of electron collision process would imply that the required condition is dependent on electron velocity and number density. While electron velocity is governed by the Maxwell's distribution of particle velocity, equation 1.2, the number density of the electron in various electronic levels  $(n_j)$  is governed by the Boltzmann distribution, equation 1.3. The number density of ions, neutrals and electrons in the plasma, under equilibrium are related by the Saha's ionization equation 1.4. As stated previously, the equilibrium distribution given by the above three equations for velocity, excitation and ionization energy is defined by a single temperature in case of LTE. Even when the radiation is allowed to escape satisfying these three conditions would necessarily require probability of inelastic collision to be significantly larger than the spontaneous emission of the radiating species. This condition can be expressed using the excitation cross-section ( $\sigma_{ii}$ ) for electrons with velocity *v* as, [9, 48–50].

$$n_e \times \sigma_{ji} v \gg A_{ji} \tag{1.5}$$

where  $A_{ji}$  is the probability of spontaneous transition from an excited level *j* to a lower level *i*.  $\sigma_{ji}$  is related to the line strength ( $S_{ji}$ ) and hence through  $A_{ji}$  following equations, 1.6 and 1.7

$$\sigma_{ji} = \left(\frac{e}{4\pi\varepsilon_0 h}\right)^2 \times \frac{\pi S_{ji}}{v^2} \tag{1.6}$$

$$S_{ji} = \frac{3}{4} A_{ji} \times \frac{(\Delta E_{ji})^3 c}{(\hbar c)^4}$$
(1.7)

where  $\Delta E_{ji}$  is the energy difference between the transition levels *j* and *i*. Substituting these two equations in the equation 1.5, we obtain the necessary condition for plasma to be in LTE as,

$$n_e \gg 1.6 \times 10^{12} T^{\frac{1}{2}} \Delta E_{ji}^3 \tag{1.8}$$

The value of  $n_e$  and T in the above equation has to be substitute in  $cm^{-3}$  and *Kelvin* respectively. In deriving the above equation, the dependence of electron velocity, v on temperature is assumed to be  $T^{1/2}$ . Throughout the course of this thesis, the LIBS spectra for various targets have been recorded in a temporal window in which the plasma parameters, T and  $n_e$  satisfy the above condition.

As mentioned previously, although this condition is necessary to ascertain the existence of LTE, it is no way a sufficient condition[11, 49]. Depending upon the target and the ambient, there are other conditions which need to be fulfilled for plasma to satisfy LTE condition. For a optically thin homogeneous LIBS plasma, the above condition may be sufficient if the relaxation time is less than the characteristic time scale of change in thermodynamic parameter, mainly temperature. For thick plasma, the self absorption effect results in considerable change in the population of ground state through radiative transition and hence use of McWhirter criterion is slightly relaxed in terms of electron number density requirement. Nevertheless, with a proper selection of acquisition window, for both the above cases, this condition can be ensured [49].

This completes the section covering all the important concepts which will serve as a foundation for procedures developed for composition estimation using LIBS. The concepts mentioned in this chapter will be used throughout the course of the present thesis.

# **1.6** Motivation and thesis overview

In the framework of a LTE plasma satisfying the conditions explained previously, the emission line intensity can be related to the number density and hence, concentration of the elements in a sample. For optically thin plasma, where self-absorption effects are negligible, this allows us to obtain a straightforward relation between these two quantities. Although an incomplete description of the actual case, this framework has been a widely used procedure for elemental analysis using LIBS since its inception. The complexity in analysis arises when one studies the plasma accounting for their optical thickness, which is a more realistic representation of the LIBS plasma. Self-absorption effects begin to kick in as the plasma opacity increases and the distortion in line profile is observed. The width of the line profile, at typical values of plasma temperature and electron number density achieved in LIBS, is mainly governed by both the self absorption broadening and broadening due to Stark effect. The latter, in-turn depends on the degree of self absorption in the plasma. The interplay of these quantities along with the uncertainty in the plasma temperature and electron number density leads to a complex relation of the observed emission line profile with the number density and concentration. Hence, the present work is motivated by the above issue of optically thick plasma so as to perform meaningful quantitative analysis from observed emission spectrum. By overcoming the limitations of the existing methods, an attempt to have a more realistic model using synthetic spectrum method relating the intensity with number density of the emitting species is made. Since, a variety of samples with multitude of elements are now being analyzed with LIBS, issues such as detection limits for minor elements and true emission line widths(Stark widths) have become relevant in recent times. Hence, it becomes important that the developed method also addresses these issues. The work presented in this thesis is mainly inspired by these topics.

The thesis has been organized as follows, first a chapter on some of the important aspects of the experimental system and analysis procedure used in this work will be presented. This will cover the details of instrument calibration, for both wavelength and intensity. This will be followed by a discussion on the common analysis methods employed for all the studies presented in the thesis which include numerical de-convolution of Voigt profile, smoothening and removal of continuum and automatic line identifications. The next two chapters will discuss spectral emissions from the plasma using radiative transfer equations and how this can be applied for quantitative estimation of elemental composition. First an account of utilising these radiative transfer equations and classical theory of spectral line emissions under LTE will be presented for optically thin plasma followed by optically thick case. An improved method for the quantitative analysis based on neutral number density of species calculated from the experimental line profiles will be presented. The method has been compared against other conventional CF-LIBS procedures.

The issue of self absorption its effect on the experimentally recorded emission lines will be a subject matter for the next chapter when discussion on synthetic spectrum generation for matching the experimental line profiles will be presented. The details of this iterative procedure will be mentioned followed by its application to obtain qualitative estimation of elemental composition from different multi-element samples. The other application of the synthetic spectrum method to estimate the detection limit for minor elements in the sample will be discussed next which will be used to explain the non-appearance of the signature for some of the species in the emission spectrum. One of the major limitations in constructing the simulated line profiles is the requirement of an exhaustive data-set for Stark parameters, hence the next chapter is devoted to a technique to experimentally determine the Stark broadening parameters. The method is based on utilising the time evolution data and the theoretical relation between the emission line parameters for optically thin and thick plasma. The method is demonstrated on a few neutral resonant lines of Aluminum.

Finally, the thesis concludes with a highlight of the major outcomes in terms of their

relevance to make CF-LIBS procedure more accurate and versatile. This chapter will also provide a glimpse of some of the future work based on the present thesis as a foundation.

# Chapter 2

# Experimental technique and analysis methods

The emission from the LIBS plasma has to be recorded with sufficient spectral resolution in a very short time window to be able to use it for any quantitative analysis. The wavelength dispersion by the spectrograph employed in LIBS study mainly decides the ability to differentiate between various atomic emission lines and hence the accuracy of element line identification. In this context, it can be easily envisaged that not only the spectral resolution but the wavelength accuracy of the spectrometer is also important for proper element identification. While identification is one part of the analysis, deriving a quantitative estimate from the spectrum is the other and perhaps the major part of analysis which requires an accurate observation of the intensity values. Hence a proper spectrometer calibration for both intensity and wavelength is of paramount importance for deducing any meaningful result from LIBS analysis.

These aspects will form a major part of the present chapter. A brief account into the experimental system and some of the data analysis methods used in the present study will be discussed. The chapter includes the calibration and expected accuracy from the spectrometer system employed for the thesis work. Various analysis procedures for data conditioning are also discussed later in this chapter which includes continuum removal from the spectrum, numerical de-convolution procedure and an automated search criteria for identifying and labeling emission lines.

# 2.1 Experimental set-up

The experimental system consists of Nd:YAG laser for plasma formation and Echelle and Czerny-Turner spectrograph, both equipped with ICCD camera for gated observations. The details of these systems are discussed in the following sub-sections.

#### 2.1.1 Laser and spectrometer

An Nd:YAG laser from Innolas laser (Spitlight 600) has been used for experiments performed during the course of work presented in this thesis. The laser is pumped using Xe-arc flash lamp at a fixed rate of 30Hz. The laser can deliver a maximum pulse energy of ~500mJ at its primary wavelength, i.e, 1064nm. Using non-linear optical crystals (KDP/BBO) for harmonic generation, laser frequency up to fourth harmonic is accessible. The beam quality factor ( $M^2$ ) for the laser system is very close to 1. The beam divergence is less than 0.5mrad and maximum temporal jitter is 1ns. The laser utilises active Q-switching by use of Pockels cell resulting in intense laser pulses of typically ~ 6ns. The Pockels cell delay decides the amount of energy stored by restricting upper energy level depletion of the lasing medium [30, 51]. It can be tuned to obtain desired pulse energy without affecting the spatial distribution of the laser pulse. This has been used in the experiment to control the enegry of laser pulse during the experiments. To synchronize the laser firing with other instruments, a TTL output signal from pockel cell trigger of the laser is provided.

The beam delivery optics from laser to the target consists of beam steering device to adjust the laser height followed by a folding mirror and a plano-convex lens of 30cm focal length. Laser beam is focused to a fine spot of approximately  $500\mu$ m at the target surface. This results in power density typically between,  $1-4\times10^{10}$ W/cm<sup>2</sup>. The beam is incident at an angle of roughly 30° from the axis of target plane and the light collection is approximately normal to the target surface.

The collection of light from plasma is preformed using the collecting optics provided by Andor Technology. It consists of achromatic collimating lens and mirror assembly, Fnumber for which is approximately 2. It has a clear aperture of 30mm and can be used to collect light from a minimum distance of 20cm in the wavelength range of 200-950nm. It is coupled to a fiber using standard SMA connectors which is fed to the spectrometer for wavelength dispersion and detection. The beam collection optics is aligned with the focal spot on the target surface by use of an alignment laser. This alignment laser operates at typically  $\sim$ 635nm with peak power less than 5mW. Initial alignment of the laser with collecting optics was performed making both the lasers overlap on the target surface.

The light from the collecting optics is brought to the spectrometer slits through optical fiber. Two kinds of spectrometers were used in the experiments, first one used for the study of thin plasma was 0.5m Czerny-Turner spectrograph from Princeton instruments. The other one used for the study of thick plasma and Stark broadening measurements was echelle spectrograph from Andor. Both these spectrographs were equipped with ultra-fast ICCD cameras. A schematic of the experimental set-up is shown in figure 2.1.



Figure 2.1: A schematic of the experimental system used for the present study.

Because of the statistical fluctuation of various parameters involved in recording the spectrum (viz., laser pulse to pulse energy variations, gain of various electronic units, MCP gain of ICCD), there is a need to average out the spectrum before it is passed for further analysis [52]. Since there is a difference in the light throughput, number of spectra to be averaged differs for both the spectrographs. While for Czerny-Turner, 20 shots were averaged, a total of few hundreds of the spectra were averaged for the echelle spectrometer. Echelle spectrometer provides the full spectrum in one shot compared with the Czerny-

Turner which provides only a portion of spectrum which falls on the detector after linear dispersion through the grating. Hence, the time and effort for recording a full spectrum in both the cases are almost similar.

A gated observation is possible with both the spectrometers because of the ICCD camera ( $1K \times 1K$ ) used in both of them. The ICCDs have micro-channel plates, HV bias for which can be pulsed very rapidly. The acquisition delay and gate width is different for different experiments and the same will be discussed for each case separately in next chapters. The ICCD gate was synchronized with the Pockels cell trigger or with a photo-diode using a digital delay generator and all of the pulses, viz., pockel cell trigger, photo-diode and ICCD gate were monitored on a digital oscilloscope. Internal delays and time jitters, if any, for any of the system were characterized and acquisition times were correspondingly compensated.

## 2.1.2 Target mount

The target for the LIBS sample was mounted on a motorized XYZ translation stage. The requirement of a translation stage is important as the target needs to be moved after a few number of laser shots fired at one spot. This is required since the heat stress at a single location results in pitting which then changes the plasma properties for successive laser shots. The translation stage used was vacuum compatible and could be mounted inside the chamber to perform target movement during experiments conducted in low vacuum levels. Some of the experiments, as will be shown in next chapters, were conducted in vacuum. A vacuum chamber of 250 mm dia with ISO 250 end flanges was used. The vacuum chamber houses the target mount and the XYZ translation stage along with the electrical feed-through required for its operation. One of the end flanges has two ISO63 quartz view-ports, one normal to the target surface (for light collection from plasma) and other one is at an angle of approximately 30° from the axis of target plane (for laser delivery). The chamber utilizes a turbo-molecular pump (520 liters/sec) backed by a dry scroll pump for creating vacuum. The transmission of the quartz window has been accounted for relative intensity correction which will be discussed in the next section.

# 2.2 Spectrometer calibration and resolution

The details of the calibration, both intensity and wavelength for the two spectrometers will be disused in this section. These calibrations are very important as the errors in the results to be presented in the next chapters largely depend on the accuracy of these calibrations. An estimate of the resolution of spectrometer will also be presented as it is an important factor for generating the simulated emission line profiles to be discussed in later chapters.

#### 2.2.1 Wavelength calibration

The wavelength calibration for both the spectrometers were carried out using the mercuryargon lamp [53]. This lamp is a low temperature discharge source which results in narrow emission lines (ideally having intrinsic line width only due to natural broadening of the emission lines) which are separated from each other by large difference in the central wavelength. The wavelength calibration for both the spectrometers were performed before the intensity correction.

Wavelength calibration of the echelle spectrograph was performed through raw echellograms. The calibration starts by locating most intense line of Hg-Ar lamp in the echelle image. By expanding the search window to include more lines from different diffraction orders, the error in wavelength calibration is reduced. This process of calibration is automated and is performed by the software provided along with the spectrometer. Typical wavelength accuracy of calibration throughout the region of interest observed in this case is better than  $\pm 0.02$ nm. The only issue with wavelength calibration of echelle spectrograph is its temperature dependence. This is because of the use of dual order prism followed by echelle grating design, which is quite sensitive to temperature. This design circumvents the problem of cross talk in the Echelle spectroscope after cross-dispersing element. Hence, the calibration needs to be performed every time the ambient temperature changes by more than 2°C so as to maintain the above value of its wavelength accuracy.

For 0.5m Czerny-Turner spectrograph, calibration was performed manually using the Hg-Ar source. Because of the limited band-pass of the system, the grating was moved to different central wavelengths every time for wavelength calibration for different spectral

regions. The wavelength shifts ( $\delta \lambda_s$ ) given by equation 2.1 showed linear increasing trend from right extreme (pixel no. 1024) to left extreme (pixel no. 0), where shift in the extreme right is negative which gradually increases and becomes positive at left extreme.

$$\delta\lambda_s(\lambda) = \lambda_{obs} - \lambda_{ref} \tag{2.1}$$

where  $\lambda_{obs}$  and  $\lambda_{ref}$  are the observed and reference wavelength respectively...

Although this shift was found to be linear (y = mx + c) with respect to pixel number  $(n_{pix})$ , its slope and intercept value changes with the reference wavelength. This can be seen from the figure 2.2 for wavelength shifts at three Hg-Ar wavelengths.



Figure 2.2: Wavelength shifts as a function of pixel number for different values of central wavelength.

Based on the above trend of shifts, the change in slope and intercept can be expressed as a function of the reference wavelength (i.e.  $m = f(\lambda)$ ). A fourth order polynomial was found to be adequate for both the quantities represented by terms  $m'_is$  and  $c'_is$  in the following equation. Hence, the final shift for central wavelength ( $\lambda_0$ ) can be obtained as,

$$\delta\lambda_s(\lambda_0) = \sum_{i=0}^4 n_{pix} \times m_i \lambda_0^i + c_i \lambda_0^i$$
(2.2)

#### 2.2.2 Intensity calibration

The intensity calibration of the echelle spectrograph was performed using deuterium-halogen (DH) lamp (Ocean Optics DH-3 plus) which provides a band spectrum from UV to NIR. The reference spectrum of the source was compared with the experimental spectrum recorded for the same. All optical elements used in the actual light collection from the plasma were introduced in between the light path during calibration to obtain comprehensive transmission characteristics. Since some of the experiments were carried out in vacuum, the viewports were introduced accordingly in the path of light from the lamp before recording for intensity calibration.

The intensity calibration was preceded by background intensity subtraction from the spectrum. The band spectrum recorded from the reference source, figure 2.3, showed rough structures in the spectrum and hence a direct normalization to obtain multiplication factors would have lead to erroneous peaks after calibration. Hence, the source spectrum recorded with the spectrometer was first smoothened using Savitzky-Golay algorithm from MATLAB<sup>®</sup>[54] in-built library as shown in figure 2.3. Moreover, the step size for wavelength obtained from the reference spectrum of the source was coarse and hence a cubic spline interpolation on the same was performed at spectrometer's wavelength interval and used for comparison.

The correction factors for relative intensity calibration were obtained by taking a ratio at each wavelength step of the source input spectrum. The factors were applied on the recorded spectrum which showed a perfect match with the source spectrum after this correction, figure 2.4

## 2.2.3 Resolution of spectrometer

One of the important factors affecting the line emission profile is the instrument resolution. The value of this instrument resolution will be used throughout the analysis presented in



Figure 2.3: Spectrum as recorded by the echelle spectrograph for DH source shown in brown color (Top panel), Reference spectrum for the DH source (blue) along with normalized and smoothened spectrum (yellow) recorded by the spectrograph (Bottom panel).

chapters 4 and 6. To estimate the instrument resolution, line emissions from Hg-Ar lamp were used. The resolution was obtained from the experimentally obtained line profiles in the wavelength region of interest. These lines emanate from low temperature and pressure arc discharge and the resultant profiles have intrinsic width dominated by natural broadening since pressure and Doppler broadening of such sources is very less. The emission lines recorded from this source showed a Gaussian profile which were fitted to obtain the line widths ( $\Delta \lambda_{inst}$ ) at different wavelengths ( $\lambda$ ). A plot of the same is shown in figure 2.5.

As can be seen from the figure, a straight line fit to the data points is possible, the slope of which gives the resolution of the spectrometer. The value of slope of the line comes out to be 0.000195 which is very close to the value of  $(\Delta \lambda_{inst}/\lambda) = 0.0002$  specified by the manufacturer.



Figure 2.4: A portion of the DH source spectrum recorded by spectrograph calibration using the correction factors. The blue line shows the source spectrum.

# 2.3 Analysis methods

Some common analysis procedures have been used throughout the course of this work and the same will be discussed in this chapter. This includes the removal of the the continuum background from the spectra and the numerical de-convolution of Voigt profile. A method to automatically search and identify emission lines will also be discussed.



Figure 2.5: Instrumental width at different wavelengths as obtained from the Hg-Ar source.

# 2.3.1 Background corrections/removal of continuum

The spectrum recorded by the ICCD spectrometer requires background subtraction before it can be used for further analysis. The two major contributing factors to the background intensity in the spectrum can be listed out as follows:

- 1. Dark noise of the CCD pixels
- 2. Continuum emission from the plasma

The dark noise of the CCD pixels can be considerably reduced by cooling the ccd pixels to lower temperatures. This is achieved through active peltier element and the spectra used in the analysis throughout this work were acquired at CCD temperature below -25°C. The subtraction of the dark noise of the CCD from the spectrum was performed by acquiring background spectrum obtained at same acquisition setting as used for plasma. An average of five spectra were used for this considering the statistical errors due to MCP gain and thermal noise.

Along with the line emissions, the plasma also emits continuum which spans throughout the wavelength range used for data acquisition. The continuum emission can be due to free-free transitions or the free-bound transitions within the plasma. The continuum due to free-free transitions are mainly due to the bremsstrahlung process in the plasma in which the electrons loses their kinetic energy in the vicinity of the electric field due to massive ions. The free-bound transitions resulting in continuum emissions are due to radiative recombination of free electrons with the ions. The continuum radiation for the former case depends on the kinetic energy of the decelerating electron as well as the energy loss in the process while for the later it depends on the electronic energy level of the recombining ion. Hence, radiation from both these processes covers the entire wavelength.

Because of the higher plasma temperature and electron number density during initial stages of the evolving plasma, the continuum emission at early time is quite significant and envelopes the line emissions [9]. Hence, the correction for the continuum becomes important for such cases. The removal of continuum from the experimental spectrum was performed after the background (dark noise) subtraction from the spectrum. A smoothing of the data over the background emission was performed using a moving average filter which was then subtracted from the spectrum. The intermittent wavelength regions where line emissions appeared were not taken into account while smoothing the background selected above a threshold intensity value. The spectrum showed different signal-to-background ratio in the wavelength range of 280-700 nm which is used to record most of the spectrum in the present thesis. The spectra were, therefore, divided in two regions(280-450nm and 450-700nm) for selection of the cut-off intensity value. An example of the same is shown in figure 2.6. The intensity calibration of the spectrum using the correction factor explained previously was performed before removing this continuum.

## 2.3.2 De-convolution procedure for Voigt profiles

A numerical de-convolution procedure developed by Abrarov et al. [55, 56] has been used to retrieve the Lorentzian and Gaussian line widths from the Voigt profiles of the recorded emission lines. The numerical procedure is rapidly convergent and results in accurate values. It is based on the Fourier expansion of the scaled complex error function w(z), the real



Figure 2.6: Background smoothening for continuum/background removal used for data correction. The background level different wavelengths is hown clearly in the inset. Spectrum is for Aluminum sample acquired at a delay of 700 ns after plasma initiation in air.

part of which is the Voigt profile, V(x,y).

$$w(z) = e^{-z^2} \operatorname{erfc}(iz) = V(x, y) + iL(x, y)$$
 (2.3)

$$V(x,y) = \frac{y}{\pi} \int_{-\infty}^{\infty} \frac{e^{-t^2}}{y^2 + (t-x)^2} dt$$
(2.4)

where, z = x + iy and the terms x and y contain the Gaussian and Lorentzian component of the line widths as shown later in chapter 4, equations 4.5 and 4.6. The term, V(x,y) can be Fourier transformed and rewritten in terms comprising of exponential multipliers which can be expanded on a valid interval,  $\tau_m$  using Fourier series.

$$V(x,y) = \sum_{n=0}^{2\tau_m - 1} \int_0^{\tau_m} \frac{a_n}{\sqrt{\pi}} e^{-y\tau} \cos(x\tau) \cos\left(\tau \frac{\pi n}{\tau_m}\right) d\tau - \frac{a_0}{2\sqrt{\pi}} \int_0^{\tau_m} e^{-y\tau} \cos(x\tau) d\tau \quad (2.5)$$

In the above equation,  $\tau_m = 12$  value results in almost negligible error in evaluating the Voigt integral [55]. The Fourier coefficients,  $a_n$  can be written as,

$$a_n = \frac{2\sqrt{\pi}}{\tau_m} e^{-\frac{n^2 \pi^2}{\tau_m^2}}$$
(2.6)

This approximation for the Voigt integral has been incorporated as a MATLAB routine to be used for de-convolution during line profile fitting routine throughout the analysis presented in this work.

# 2.3.3 Automatic line identification by evaluating intensities at T = 1 eV

The need for an automated line search and identification procedure becomes clear when analyzing data from multi-element samples consisting of hundreds of emission lines. An unambiguous identification of the emission lines for such samples is necessary for an accurate and reliable retrieval of elemental composition. The analysis of spectrum, in such cases is complex because of the presence of a large number of lines in the vicinity. It may also happen that some transitions have a similar value of the central wavelength and hence a proper labeling of such lines pose a serious challenge. To resolve such cases, a straightforward approach of evaluating peak line intensities from different transitions of a particular species at a temperature of 1eV is used. For this, the following equation considering optically thin plasma is used,

$$I_{\lambda}^{j \to i} = \alpha \frac{g_i f_{ij}}{\lambda^3} \times \exp\left(\frac{-E_j}{k_B T (= 1eV)}\right)$$
(2.7)

where  $g_i$ ,  $f_{ij}$  and  $E_j$  are the statistical weight oscillator strength and energy level for the transition from upper electronic level *j* to lower level *i*.  $\alpha$  is a constant factor term (includes instrument factor and other atomic constants) for all lines belonging to the same species. Since, the relative emission intensity of these transitions depends on the individual values of oscillator strengths, upper state energy level and the plasma temperature, this approach to sort the lines based on their expected intensities seems logical.

A sub-list of the most prominent lines for each species in the plasma arranged in descending order of intensity can then be made from an exhaustive database of the atomic transitions. From this sub-list, a few most prominent lines are selected at first for each species and assigned to the identified lines in the spectrum. The search window is then increased by increasing the number of lines till most of the emission lines in the experimental spectrum are identified and labeled. The value of the temperature (1 eV) used for creating this list is only a typical value and it has no relevance to the actual plasma temperature which is obtained through methods discussed later in chapter 3 and 4. The method has been used for line identification during analysis of the spectral data throughout this thesis. The method proved quite helpful while analyzing the data of steel and rock samples which had dense spectrum.

The above anlysis methods, viz., background corrections, numerical deconvolution of Voigt profile and automatic line identification are primary steps before they are used for further analysis.

# Chapter 3

# Ratio based algorithm for optically thin plasma spectrum

As discussed in the previous chapters, the quantitative estimate using CF-LIBS procedure requires plasma to be in LTE. By properly selecting the acquisition time window, this condition is generally met in the experiment. Assuming a homogeneous plasma, the emissions coming from the plume can be obtained using the radiative transfer equation. Depending on the plasma opacity, the resultant intensity falling on to the spectrometer can be obtained by either considering the plasma to be optically thin or thick. Using the CF-LIBS approach, the present chapter presents a method which assumes an optically thin plasma to obtain the elemental concentration from metal samples. The optically thick case, which will include the self absorption effect, will be a subject matter for the next chapter.

Although setting up of relevant equations for relating the concentration of element from line intensities for optically thin plasma is relatively straightforward, it actually lays down almost all essential concepts used in the CF-LIBS approach. Hence, a discussion of the optically thin plasma case is important for completeness of the procedure. Therefore, the present chapter is devoted to a discussion on an improved ratio based procedure [57] developed to obtain quantitative estimates assuming an optically thin LTE plasma. The work presented in this chapter is an extension over the work of Ciucci et al. [26] and Gomba et al. [58], two widely used CF-LIBS algorithms for quantitative analysis. The suitability of such CF-LIBS procedures for quantitative analysis has been successfully demonstrated by

various groups on different samples [59, 60]. The relation between emission line intensity from optically thin plasma and concentration of the corresponding element will be derived in this chapter followed by an iterative scheme to retrieve the concentration values from neutral number densities. A comparison of the performance of improved ratio based algorithm with the above two approaches will also be presented in the concluding section of the present chapter.

# **3.1** Radiative transfer equation for thin plasma

The emission from optically thin homogeneous plasma under LTE can be quantified in terms of the emission coefficient,  $\varepsilon_{\lambda}$ , such that [23, 61],

$$I_{\lambda}^{\dagger} = \varepsilon_{\lambda} \times l_{abs} \tag{3.1}$$

where,  $I_{\lambda}^{\dagger}$  is the emission line intensity for thin plasma and  $l_{abs}$  is the path length. The value of  $\varepsilon_{\lambda}$  for a transition from upper electronic state *j* to a lower state *i* can be expressed as,

$$\varepsilon_{\lambda} = \frac{1}{2} \times n_j A_{j \to i} \frac{hc}{\lambda_0} \Omega(\lambda)$$
(3.2)

where,  $n_j$  is the number density of the upper state,  $A_{j\to i}$  is the transition probability of spontaneous emission for  $j \to i$  transition and  $\lambda_0$  is the central wavelength of transition.  $\Omega(\lambda)$  is the normalized emission line profile, which gives the probability of emission of photon of width  $\delta\lambda$  about the central wavelength  $\lambda_0$ .

Assuming a Boltzmann distribution of electrons in the atomic levels of emitting species, the number density of the upper state *j* can be written as,

$$n_j = \frac{n_k g_j}{U_k(T)} \times \exp(\frac{-E_j}{k_B T})$$
(3.3)

where,  $n_k$  and  $U_k(T)$  is the number density and partition function of species k in the plasma at temperature T.  $k_B$  is the Boltzmann constant and  $g_j$  represents the statistical weight of the upper energy level j. The partition function,  $U_k(T)$  is obtained as,

$$U_k(T) = \sum_i g_i \exp(-\frac{E_i}{k_B T})$$
(3.4)

The transition probability  $A_{j\rightarrow i}$  in equation 3.2 can be expressed in terms of the oscillator strength for the transition  $f_{ij}$  as [62],

$$A_{j \to i} = \frac{2\pi e^2}{m_e c \varepsilon_0} \frac{g_i}{g_j} \frac{f_{ij}}{\lambda^2}$$
(3.5)

The oscillator strength values from various databases have been used for the present study and hence this substitution is advantageous. Using equations 3.1, 3.2, 3.3 and 3.5, integrated line intensity  $(\tilde{I}^{\dagger}_{\lambda})$  for the above transition can be written as,

$$\tilde{I}_{\lambda}^{\dagger} = F_{inst} \frac{n_k g_i f_{ij}}{U_k(T)\lambda^2} \times \exp\left(\frac{-E_j}{k_B T}\right)$$
(3.6)

The  $F_{inst}$  term in the above equation is a constant factor which takes into account the instrument functions and all other physical constants.

# 3.2 Ratio based algorithm

This section discusses the procedure used for the quantitative analysis with the obtained line emission spectrum. As mentioned in the previous chapter, the plasma is assumed to be homogeneous and in LTE. The intensity relation derived previously for optically thin plasma will be utilized to relate the plasma parameters to retrieve elemental concentration.

### **3.2.1** Methodology

Equation 3.6 can be rearranged to express the number density of  $k^{th}$  species in terms of the recorded line intensity as,

$$n_k = \frac{\tilde{I}_{\lambda}^{\dagger} \lambda^2}{g_i f_{ij}} \times \frac{U_k(T)}{F_{inst}} \times \exp(\frac{E_j}{k_B T})$$
(3.7)

Hence, number density of any species in the plasma can be obtained from the integrated line emission intensity once the value of plasma temperature, T and  $F_{inst}$  is known. Considering species only up to third degree of ionisation to be present in the plasma, for  $m^{th}$  element in an n element sample, the concentration can then be simply obtained as,

$$c_m = \frac{\sum_{i=0}^3 n_m^i}{\sum_{j=1}^n \sum_{i=0}^3 n_j^i}$$
(3.8)

The signature of emission lines from ionized species are in general weak and it may occur that in a multi-element sample, the signature of ionized species from some of the elements may not be present. In such cases, their number densities can be obtained using Saha ionisation equation once the electron number density is known.

$$\frac{n_m^{II}}{n_m^{I}}n_e = \left[\frac{(2\pi m_e k_B)^{\frac{3}{2}}g_e}{h^3}\right]T^{\frac{3}{2}}\frac{U_m^{II}(T)}{U_m^{I}(T)} \times \exp\left(-\frac{\chi^I}{k_BT}\right)$$
(3.9)

where, the subscripts I and II represent the neutral and first ionic state respectively and  $\chi^{I}$  represents the first ionisation potential of the element *m*. The term  $g_{e}$  is the Landé splitting factor whose value is taken as 2. The electron number density,  $n_{e}$  can be obtained from the spectrum by using the above equations 3.7 and 3.9 once we have emission intensity for neutral and ion species for at least one of the elements.

As is evident from the previous discussions, to retrieve the number densities, we require a prior knowledge of plasma temperature. The plasma temperature can be obtained using Boltzmann plot method which employs equation 3.6 and is discussed below.

### **Boltzmann plot method**

The intensity relation in equation 3.6 can be rearranged as,

$$\left(\frac{\tilde{I}_{\lambda}^{\dagger}\lambda^{2}}{g_{i}f_{ij}}\right) = \frac{F_{inst}n_{k}}{U_{k}(T)} \times \exp\left(-\frac{E_{k}}{k_{B}T}\right)$$
(3.10)

Taking natural logarithm on both sides of the above equation we have,

$$\log\left(\frac{\tilde{I}_{\lambda}^{\dagger}\lambda^{2}}{g_{i}f_{ij}}\right) = \log\left(\frac{F_{inst}n_{k}}{U_{k}(T)}\right) - \left(\frac{1}{k_{B}T}\right) \times E_{j}$$
(3.11)

A plot of upper state levels  $E_j$  corresponding to different transitions for same species versus the term on the left hand side of equation 3.11 is called the Boltzmann plot [26, 60, 63, 64]. The slope of the this plot gives the value of plasma temperature. A plot for the case of Cu I species in a plasma formed from brass sample will be shown later in this chapter when the application of the above procedure is discussed.

The only unknown parameter required to estimate the individual number densities and hence concentration is the constant factor,  $F_{inst}$  appearing in equation 3.6. Since, this factor

is assumed to be constant for all the species, by taking a ratio of the number densities, and utilizing the plasma neutrality condition, individual number densities can be obtained. An algorithm developed to perform this is explained in the next section.

## 3.2.2 The algorithm

The procedure to retrieve number density of different species in the plasma proceeds by obtaining the integrated line intensities from the observed spectrum. For this, numerical de-convolution procedure as discussed in section 2.3.2 of previous chapter is used. From the de-convolved Voigt profile, once the values of Lorentzian and Gaussian component of line widths and peak intensity are obtained, a numerical integration is performed on the relevant wavelength region for each identified transition. From these values, the plasma temperature is obtained using the Boltzmann method and observed electron number density  $(n_e^{obs})$  is calculated using the Saha equation 3.9.

A successive ratio of neutral number densities using equation 3.7 is then calculated based on the previously derived values of temperature and electron number density. Hence, for an *n* element sample we obtain n - 1 ratios given by,

$$r_i = \frac{n_i^I}{n_{i+1}^I}$$
(3.12)

The values for these n - 1 ratios  $r_1$ ,  $r_2$ ,  $r_3$ ,.....  $r_{n-1}$  can be determined once  $n_e$  and T is obtained. The estimation of number densities of all species from these  $r_i$ 's is performed through iterative procedure. A value of neutral number density for the first element is assumed and from the successive ratio terms,  $r_i$ 's, neutral number density for all other elements are obtained. Based on these neutral number densities, ionic number density is obtained for all the species using Saha equation. The value of electron number density is then once again calculated ( $n_e^{cal}$ ) utilizing the plasma neutrality condition. The value of  $n_e^{cal}$  at any iteration step is then given by the following expression,

$$n_e^{cal} = \sum_{i=1}^{n} \sum_{j=1}^{z} j \times n_n^j$$
(3.13)

where, *n* is the number of elements and  $n_n^j$  represents the number density of  $n^{th}$  element of ionisation *j*. *j* = 1 corresponds to the first ionisation state.

The value of calculated electron number density  $n_e^{cal}$  is then compared with the observed value,  $n_e^{obs}$ . The error in this is expressed as,

$$\varepsilon = n_e^{cal} - n_e^{obs} \tag{3.14}$$

The initial assumption of neutral number density for the first element is then varied based on this error and once again  $n_e^{cal}$  is obtained using plasma neutrality condition with update number density values. The process continues till a convergence within a set tolerance value is achieved.



Figure 3.1: Ratio based algorithm to retrieve elemental concentration for optically thin plasma

A flowchart of the algorithm is presented in figure 3.1. The final values of number density obtained from the above algorithm is then used to obtain the concentration using equation 3.8. The algorithm is implemented as different MATLAB routines and performs all the tasks automatically after peak identification.

# **3.3** Verification of the developed procedure

To verify the developed scheme, an experiment was conducted on brass sample. The results obtained from this method is also compared with other traditional CF-LIBS method. A brief account of which is presented later in this section. The experimental set-up described in previous chapter was used to acquire the spectrum of the brass sample. A brief detail of the experimental parameters is mentioned in the following sub-section.

# 3.3.1 Experimental details

A 0.5m Czerny-Turner spectrograph equipped with an ICCD camera was used for this study. The details of the calibration, both intensity and wavelength has been discussed in detail in the previous chapter. The sample used in this experiment is obtained from BS 249 brass rod. The experiment was conducted in vacuum with an ambient pressure of  $2 \times 10^{-2}$  mbar. The emission from the plasma was recorded normal to the target mounted on a motorized XY stage inside the chamber. A gate width and gate delay of 200ns was used for this experiment. The background continuum from the plasma was negligible at this delay. Laser shots were fired using primary wavelength of Nd:YAG laser and typical fluence in the experiment was 15 J/cm<sup>2</sup>. Various triggers and timings of the ICCD were controlled using digital delay generator with typical jitter of the order of 1ns.

The emission spectrum was acquired for a wavelength range of 320-680 nm. Spectra from 20 laser shots were averaged for each wavelength span of the spectrometer after which target was moved to provide fresh surface for next reading. These acquisition shots were preceded by 5 laser shots on the target for cleaning. The spectrum obtained for each wavelength span was calibrated for its wavelength and intensity before stitching was performed to obtain a continuous spectrum.

A part of the obtained spectrum for the brass sample with some of the species identified is shown in figure 3.2. From this spectrum, an automated routine performs peak identification followed by comparison with atomic databases [65] and [66]. Emission lines corresponding to Cu I, Cu II and Zn I were identified from the spectrum. List of emission lines used in the present analysis along with the associated atomic parameters is given in Appendix A.1.

From the deconvolved profiles obtained using the method discussed in section 2.3.2, peak fitting is performed on all of the identified peaks. This is shown in figure 3.3 for some of the lines in the spectrum. The calculation of the plasma parameters, T and  $n_e$  based on this will be discussed in the next section.



Figure 3.2: A portion of the obtained spectrum for Brass with some of the identified lines used in the analysis

# 3.3.2 Evaluation of plasma parameters

As mentioned in the algorithm, figure 3.1, before proceeding to the iterative steps, we need to obtain the value of plasma temperature and electron number density. The plasma temperature is obtained using the Boltzmann plot method discussed in the previous section. The plasma temperature was obtained using the emission line from neutral copper. Boltzmann plot for the same is shown in figure 3.4. The plasma temperature obtained from the slope of the plot comes out to be  $\sim 11300 K$ .

Once the value of plasma temperature is obtained, calculation of electron number density is straightforward and is performed using the Saha ionisation equation 3.9. Since only ionic signature from Cu II could be observed from the spectrum, the calculation for  $n_e$  is



Figure 3.3: Voigt profile fit to some of the identified lines in the brass spectrum. The value of Lorentzian width,  $\omega_L$  and Doppler width,  $\omega_D$  is also shown for each profile.

done by taking a ratio of number densities of Cu I and Cu II. The value of electron number density is obtained as,  $\sim 3.3 \times 10^{15} \ cm^{-3}$ .

To verify whether the plasma satisfies LTE condition given by the McWhirter criterion discussed in section 1.8, the obtained values of plasma temperature and electron number density are substituted in equation 1.8. The value exceeds the limit mentioned in equation 1.8 and hence the plasma can be safely assumed to be in LTE.

The individual number densities are then evaluated using the iterative procedure described previously. From the value of the final iteration, the concentration estimates are then obtained for the brass sample. The results of this are presented in the next section where the same will be compared with other CF-LIBS algorithms.

## **3.3.3** Comparison with other methods

The final estimate of concentration for the brass sample using this method is shown later in table 3.1. The present scheme is compared with two conventional algorithms generally used for CF-LIBS to show its competence. These algorithms are briefly discussed in the



Figure 3.4: Boltzmann plot for plasma temperature estimation using Cu I emission lines of the brass sample. The temperature is obtained using the slope of the straight line fitted on to experimental data points.

subsequent section.

#### 3.3.3.1 Ciucci's algorithm

CF-LIBS procedure has its inception with the algorithm proposed by Ciucci et al. [26]. Apart from the temperature estimation using Boltzmann plot, this procedure also utilizes the plot to obtain the concentrations from the intercept. The intercept of the plot given by,  $\log\left(\frac{F_{inst}n_k}{U_k(T)}\right)$  from equation 3.11 is used to find  $F_{inst}n_k$  for different species once the temperature is known. The instrument factor, in this case is modified so as to write the intensity relations in terms of  $\tilde{F}_{inst}c_k$  where  $c_k$  represents the concentration value of the  $k^{th}$ species. This constant factor is retained till end and is obtained by utilizing the following relations,

$$\sum_{i=1}^{n} \sum_{j=1}^{z} c_n^j = 1$$
(3.15)

Element	Present	Ciucci's	EPMA
	Algorithm	Algorithm	
Cu	68.0	67.1	68.4
Zn	32.0	32.9	31.6

Table 3.1: Concentration estimates for brass sample using different methods

where,  $c_n^j$  represents concentration of  $j^{th}$  ionisation of  $n^{th}$  element. Hence, using above normalization, the instrument factor is obtained as,

$$\sum_{i=1}^{n} \sum_{j=1}^{z} \tilde{F}_{inst} c_n^j = \tilde{F}_{inst}$$
(3.16)

Individual concentrations are then estimated by dividing each  $\tilde{F}_{inst}c_k$  by the derived value of instrument factor  $\tilde{F}_{inst}$ .

#### 3.3.3.2 Gomba's algorithm

This algorithm was proposed by Gomba et al. [58]. It is also based on the number density ratios but differs in that the ratios are computed from total number density instead of the neutral number density considered in the present scheme. Moreover, at each iteration total number densities for all elements are varied simultaneously satisfying the line intensity ratios observed in the experiment as well as the plasma neutrality condition. Hence, two iterative loops are required to satisfy both these conditions.

#### **3.3.3.3** Advantage of the present scheme

The results obtained from Ciucci's algorithm is also shown in table 3.1. Gomba's algorithm [58] will result in the same value as obtained from the present method because of similar nature of iterations involved in calculation of number densities. The results are compared with the EPMA measurements carried out on the same sample. The results obtained from the present scheme is clearly in better agreement with the EPMA measurements compared to the Ciucci's algorithm. This can be understood in terms of the different approach for

concentration estimate followed in Ciucci et al. [26] compared to the present method. The calculation of concentration using exponent of the intercept from Boltzmann plot introduces larger errors when compared with the ratio based algorithm. Comparing present method with Gomba'a algorithm, although both are ratio based and result in same concentration values, the later scheme is more computationally expensive since number density of all elements changes simultaneously while in the present scheme number density of only first element is changed. The other densities are automatically obtained from the experimentally obtained ratios. Hence, the convergence in the present method is faster. The advantage of the present scheme over other methods is hence established.

# Chapter 4

# Synthetic spectrum method

The work presented in the previous chapter describes the case when the plasma is in LTE and is optically thin. Although such an analysis results in a reasonably good estimate of the concentration values, more general case for LIBS plasma is when the self absorption in the plasma is dominant resulting in distortion of the line profile. This significantly affects the final estimates obtained from the method presented in the earlier chapter. By correctly accounting for the self absorption effects, the assumption of optical thinness of the plasma is no longer necessary. This will lead to much better estimates for concentration for multielement samples in which most of emission lines corresponding to the major elements are self absorbed. There have been several attempts to do this. One of the most common approach is curve of growth technique first demonstrated for LIBS analysis by Bulajic et al, [67] followed by Aragón and Aguilera [68]. By calculating curve of growth (absorption as a function of number density and oscillator strength) at different degrees of self absorption, the experimentally obtained emission line profiles are corrected. It may be noted here that the self absorption effects not only affect the peak intensity but also affects the line widths which are otherwise broadened only due to Stark effect. The broadening due to self absorption at different values of number density can be seen from simulated line profiles shown in figure 4.1.

To model the plasma for inclusion of the self absorption effects, various schemes have been proposed. A post-breakdown model of the plasma evolution has been developed by Gornushkin et al. [69, 70] to estimate the plasma parameters at different evolution



Figure 4.1: Simulated profiles demonstrating line broadening due to self absorption evident by increasing number density (in  $cm^{-3}$  shown in legends) for a emission line of neutral aluminum. The intensities are normalized to a common maximum value.

times. The model takes into account the radiation dynamics of the plasma from an initial guess value of the temperature and electron number density for which the plasma is assumed to reach LTE immediately after its formation. Hence, self absorption and plasma in-homogeneity is incorporated automatically in this method. By performing a simulated annealing optimization of the initial plasma parameters to match the experimental spectrum, final estimates for concentration, temperature and electron number density are obtained. Because of the Monte-Carlo technique of optimization used in this method, the method is commonly referred to as MC-LIBS [70]. Instead of developing a complete radiation dynamics model starting from plasma formation, another approach utilizing the classical theory of spectral line emissions from plasma in LTE has been demonstrated by Yaroshchyk et al. [71] and Gerhard et al. [72]. The synthetic profiles for the the LTE plasma are constructed considering radiative transfer equations and matched with the experimental spectrum.

The work presented in this chapter is motivated by some of the limitations of the previ-

ously described schemes[73]. The MC-LIBS procedure is computationally expensive and the results shows good agreement only for initial time (few hundreds of ns) after plasma formation [71, 74]. Becuase of the larger time and resource requirements, the Monte-Carlo approach is used only on a few emission lines which sometimes results in more errors compared to the conventional LIBS method [74]. Although some recent works utilizing GPU based parallel computing has reduced the computational time drastically [75], but the requirement of even bigger computational facility makes it a less favorable option. In the synthetic spectrum method, while the work by Yaroshchyk et al.[71] does not take into account the self absorption and Stark broadening for majority of emission lines, the scheme presented by Gerhard et al. [72], necessitates avoidance of optically thick and merged lines. As a result, fewer lines are used in the analysis which provides only semi-quantitative results from these methods.

The analysis method presented in this chapter is based on the method discussed above. Simulated line profiles are obtained considering radiative transfer equation for optically thick plasma which is then fitted on to the experimental spectrum to retrieve various plasma parameters which includes concentration, temperature and the number densities. By including large number of emission lines and correctly accounting for self absorption, an attempt to overcome some of the limitations of the previously discussed methods has been made. The present scheme of analysis also accommodates an automated search for emission lines from a vast atomic database to compare with the experimental spectrum. To minimize error due to manual selection of lines and analysis [71], the present method has minimal manual intervention from initial line identification to final composition determination. The method has been applied to different multi-element samples, the results for which will be discussed later in this chapter.

# 4.1 Radiative transfer equation for thick plasma

The following derivations assumes the plasma to be homogeneous and collisionally averaged. The spectral irradiance of an optically thick LTE plasma of length  $l_{abs}$  from the classical theory of emission lines considering self absorption is given by [51, 61, 67],

$$I_{\lambda}^{ji} = F_{inst} \int_{0}^{l_{abs}} \varepsilon_{\lambda}^{ji}(l) \exp\left(-\int_{l}^{l_{abs}} \kappa_{\lambda}^{ji}(l') dl'\right) dl$$
(4.1)

where,  $\varepsilon_{\lambda}^{ji}(l)$  represents the emission coefficient of line corresponding to transition from energy level  $j \to i$  for a thin layer of thickness dl at length l from the plasma starting point, the value for this is given by equation 3.2. The term,  $\kappa_{\lambda}^{ji}(l')$  is the absorption coefficient for a thin layer in the plasma whose value is given by,

$$\kappa_{\lambda}^{ji} = \kappa_0 \frac{a}{\pi} \int_{-\infty}^{+\infty} \frac{e^{-t^2}}{(t-x)^2 + a^2} dt$$
(4.2)

Note that this term includes the line profile function,  $\Omega(\lambda)$ , appearing in equation 3.2 as a convolution of the Gaussian and Lorentzian components of the line width. If the plasma is considered as homogeneous, the term  $\kappa_{\lambda}^{ji}$  is independent of the absorption path length. In that case, equation 4.1 can be simplified as,

$$I_{\lambda}^{ji} = F_{inst} \frac{\varepsilon_{\lambda}^{ji}}{\kappa_{\lambda}^{ji}} \times \left(1 - \exp(-\kappa_{\lambda}^{ji} l_{abs})\right)$$
(4.3)

The value of absorption path length,  $l_{abs}$ , is generally written in CGS units and hence the value of terms appearing on right hand side of equation 4.2 for  $\kappa_{\lambda}^{ji}$  can be written as,

$$\kappa_0 = \frac{2e^2 f_{ij} n_i \sqrt{\pi \ln 2}}{mc^2} \left(\frac{\lambda^2}{\Delta \lambda_G}\right)$$
(4.4)

$$a = \sqrt{\ln 2} \frac{\Delta \lambda_L}{\Delta \lambda_G} \tag{4.5}$$

$$x = 2\sqrt{\ln 2} \left(\frac{\lambda - \lambda_0}{\Delta \lambda_G}\right) \tag{4.6}$$

where  $\Delta\lambda_G$  and  $\Delta\lambda_L$  are the Gaussian and Lorentzian components of the line width. All other terms have the same explanation as mentioned in the previous chapter. The value of constant 'e', i.e., electronic charge in the above equation is in statcoloumbs. Assuming a Boltzmann distribution of the electrons, line intensity equation for thick plasma case given by equation 4.3 can be rewritten using equation 3.2, 3.3 and 4.2 as,

$$I_{\lambda}^{ji} = \frac{\tilde{F}_{inst}}{\lambda_0^5} \exp\left(-\frac{E_j - E_i}{k_B T}\right) \left[1 - \exp(-\kappa_{\lambda}^{ji} l_{abs})\right]$$
(4.7)
$$\kappa_0 = \frac{2e^2 g_i f_{ij} n_0 \sqrt{\pi \ln 2}}{mc^2 U(T)} \left(\frac{\lambda^2}{\Delta \lambda_G}\right) \exp\left(-\frac{E_i}{k_B T}\right)$$
(4.8)

The instrument factor term has been modified in equation 4.7 to include all constant terms. This equation gives the intensity of the line emission for optically thick LTE plasma. The method described in this chapter is based on this equation and will be discussed in detail in the next section.

# 4.2 Synthetic spectrum generation

Once the value of line intensity for optically thick plasma incorporating the effect of self-absorption is obtained, synthetic emission profiles for different transitions of various species can be constructed. This will require the value of various parameters appearing in equation 4.7. Before doing that, a classification of these parameters are important to understand how these affect the full spectrum in multi-element sample.

#### **4.2.1** Classification of parameters

The parameters appearing in equation 4.7 can be classified based on how they influence the general appearance of the line spectrum. For example parameters such as  $\tilde{F}_{inst}$  affects the overall intensity of the spectrum and can be simply manipulated to normalize the simulated spectrum to match with the experimental one. On the other hand, parameters such as oscillator strength,  $f_{ij}$  affects only a specific transition for a particular species deciding profile for a particular line emission.

Table 4.1 lists out all the parameters required to evaluate the line intensity along with their classification. The local parameters include emission line specific inputs such as atomic parameters of the line, central wavelength and the two components of the line width. The semi-local parameters are inputs which are constant for all the line emissions for a particular species. This includes the total number density and partition function evaluated at a temperature T for a particular species. Finally, the global parameters include all inputs which remain constant for all emission lines from various species in the plasma and this

includes, instrument factor, absorption path length and the plasma temperature.

Local parameters	Semi-local parameters	Global parameters
$g_i, g_j, f_{ij}, E_i, E_j, \lambda_0, \Delta\lambda_G, \Delta\lambda_L$	$U(T), n_0$	$ ilde{F}_{inst}, l_{abs}, T$

Table 4.1: Classification of parameters to be used for generating simulated intensity profile

Values of local parameters except the line widths values are easily accessible from various atomic databases such as [65, 66] which have been extensively used in this thesis. The estimation of value of other parameters will be discussed in the next section.

# 4.2.2 Estimation of various parameters

This section deals with the calculation of the parameters listed out in table 4.1 which are otherwise not readily available.

#### 4.2.2.1 Gaussian component of emission line width

The Gaussian component in the Voigt profile given by equation 4.2 is mainly due to the instrument broadening and the Doppler effect. The Doppler broadening of the emission lines is due to thermal motion of emitting species and as discussed in section 1.5.3 of chapter 1, the velocity distribution is assumed to be Maxwellian. In that case, the Doppler width at a temperature T for emitting species of mass m can be obtained as,

$$\Delta\lambda_G = \lambda_0 \left( 8(\ln 2) \frac{k_B T}{mc^2} \right)^{\frac{1}{2}}$$
(4.9)

By substituting typical value of plasma temperature ( $\sim 1 \text{ eV}$ ) for LIBS in the above equation, we can easily verify that its value is well below 0.01nm for emitting species of mass > 10 amu. Hence, the contribution of Doppler broadening to the emission line width will be neglected in all our further analysis.

The other major factor affecting the Gaussian width of the line is due to instrumental broadening. This includes the transfer functions for all the elements used for recording the plasma emission. An estimate of the instrumental broadening utilizing line emissions from a low temperature mercury-argon source has already been explained in section 2.2.3, the value of which has been used throughout the analysis followed in this work.

#### **4.2.2.2** Lorentzian component of emission line width

The Lorentzian component is mainly governed by the Stark broadening of the line profile originating from the plasma. Although a much more detailed discussion will be presented later in chapter 6, an alternate approach for an approximate estimation of Stark widths is presented in this section. Self absorption contributes to both the Lorentzian and Gaussian component of the line width but as explained in the previous section, since the intrinsic Gaussian width of the emission lines are very less, broadening of the Gaussian profile due to self absorption can be safely neglected. The contribution of the self-absorption broadening to the Lorentzian component is considerable and hence is included in the analysis.

The self-absorption broadening of the profile in-turn depends on the Stark broadening of the emission lines. Therefore, a direct estimation of the self absorption from experimental line profiles originating from optically thick plasma is not possible. Stark broadening can be obtained using Stark parameters once value of electron number density (as discussed in next chapter, equation 6.15) is available. Non-availability of these parameters for various emission lines in multi-element samples aggravates the problem of estimating actual line widths. It may be noted here that if the plasma is optically thin (no self-absorption), an estimate of the true Lorentzian width (which is only due to Stark broadening) can be obtained by a direct fitting of the line profiles with a Voigt function.

To obtain true line widths for optically thick plasma, an iterative procedure suggested by [67] utilizing a self absorption parameter (SA) given by equation 4.10 has been used. The method has been successfully verified for case of a few manganese lines in the work reported by Bredice et al. [47].

$$SA = \frac{I_{exp}}{I_{thin}} \tag{4.10}$$

where,  $I_{thin}$  is the emission line intensity for optically thin plasma calculated using equation 3.6 and  $I_{exp}$  is the experimentally obtained peak intensity value. This SA parameter is also

related to the true line width through the following equation,

$$SA = \frac{\Delta \lambda_{true}}{\Delta \lambda_{exp}} \tag{4.11}$$

To evaluate the associated errors with this method, a synthetic emission spectrum using the procedure described in the next section is generated for brass sample for both thin and thick plasma with input parameters as shown in table 4.2. The value of Lorentzian width was chosen randomly between 0.01 nm to 0.16 nm for a set of emission lines corresponding to Cu and Zn. The iterative procedure starts with an input value of Lorentzian width as obtained from line profile fitting routine for the Voigt profile. Using this value of  $\Delta\lambda_L$ , the SA parameter is obtained using equation 4.10. Once the value of SA is known, it is used in equation 4.11 to correct the value of  $\Delta\lambda_L$  as input to the model. Using this updated value, next iteration is performed which results in successive correction to obtain true line widths.

Table 4.2: Input parameters used for generating synthetic emission spectrum

Temperature (T)	Electron number density $(n_e)$	Concentration (C)	
14000 K	Thin case: $3 \times 10^{15}$ cm <sup>-3</sup>	Cu: 56%	
	Thick case: $3 \times 10^{16}$ cm <sup>-3</sup>	Zn: 44%	

To verify this iterative procedure, simultaneous fitting of emission lines using the value of  $\Delta\lambda_L$  obtained from direct Voigt profile fitting for optically thin case ( $n_e = 3 \times 10^{15} \text{ cm}^{-3}$ ) was preformed. The final values of the plasma parameters as well as true line widths perfectly matches with each other. Thereafter, the case of optically thick plasma was considered and iterative scheme suggested above was used. Table 4.3 and Figure 4.2 lists out the value of plasma parameters and error in the estimation of line widths at each iteration steps.

As can be seen from the figure 4.2, the error in estimation of line width decreases considerably after 4 iterations. Hence, this scheme will be adopted in the synthetic spectrum algorithm discussed in the next section.

This completes all set of local parameters required for obtaining the simulated line profiles. Next, a discussion on estimation of semi-local parameters will be presented.

	Condition	Thin plasma	Thick plasma, iteration #				
			1	2	3	4	5
	T, in K	14046	13876	13959	13979	13985	13987
	$n_e$ , in ×10 <sup>16</sup> cm <sup>-3</sup>	0.32	2.58	2.85	2.92	2.94	2.95
	$C_{Cu}$ , in %	55.91	55.49	55.69	55.74	55.75	55.76
	$C_{Zn}$ , in %	44.09	44.51	44.31	44.26	44.25	44.24

Table 4.3: Estimated plasma parameters obtained after fitting the simulated profile for various cases

#### 4.2.2.3 Partition function

The partition function, U(T), equation 3.4, for any species is a sum over all possible energy state and is a function of temperature. The iterative procedure requires temperature value to be updated at each iteration step. The calculation of the value of partition function for each step is quite cumbersome. To resolve this, a database of partition function at predetermined temperature values is created using the NIST [65] database for atomic energy levels. The calculation of partition function during iterations at any other temperature is then performed using interpolation on this data set. This is possible because of the smooth dependence of partition function on temperature, figure 4.3. For elemental analysis carried out using this method, a database of partition function was made for a temperature range of 0.5eV - 1.5eV which is generally the range for LIBS plasma. The values are stored at an interval of 0.05eV.

To verify the effectiveness of the interpolation scheme, partition function obtained using interpolation on the database was compared with the actual values obtained from NIST database. The relative error in the estimation was always found to be less than 0.1%.



Figure 4.2: Error in estimation of true line widths using iterative scheme for various cases for a few emission lines. Error obtained at the end of each iteration(1,2,..) is also shown.

#### 4.2.2.4 Number density for different species

Inputs required to generate simulated spectrum consist of plasma temperature, electron number density and the concentration values. The derivation of number density for different species to be used for calculating line emission intensity, equation 4.7, from these three parameters is not straightforward. This is mostly because of the ionisation ratio are different for different elements at any given temperature and electron number density. This ratio is governed by the Saha's ionisation equation for LTE plasma and is given by equation 3.9. To obtain number densities for a given value of T,  $n_e$  and C, an iterative procedure (figure 4.4) is followed which satisfies both Saha's equation and the plasma neutrality condition.

The iterations start with an initial assumption for total number density of the elements and based on the input concentration value, individual number densities for each element are calculated. This is followed by a second assumption for neutral number density for each element. For starting point, a value of 10% of the corresponding elemental number density



Figure 4.3: Variation of partition function (U(T)) with temperature for neutral and ionic iron.

is taken for the neutral number density. Once we have this value, using Saha's ionisation equation ionic number densities are evaluated for each element at input value of T and  $n_e$  up to third ionisation stage. The sum of neutral and ionic number densities are compared with the individual total number density for each elements. If there is a mismatch, the assumed value of neutral number density is adjusted in the next iteration. Once, an agreement is reached for input and calculated value of neutral number density, total electron number density is evaluated using plasma neutrality condition and compared with the input value. If the values are not matching, the initial assumption of total number density is adjusted and whole iterative steps are repeated till we achieve an agreement. The flowchart for the iterative scheme presented here is shown in figure 4.4.



Figure 4.4: Flowchart of iterative procedure to obtain individual species number density from a given value of  $[T, n_e, \text{ and } c]$ .

Figure 4.5 shows typical convergence of this iterative procedure for a stainless steel sample used in the present study to determine the number density of various species in the plasma for a given value of C, T and  $n_e$ . The simulated spectrum utilising the number density values obtained through this method will be shown later in the next section, figure 4.6.



Figure 4.5: Variation of normalized error with iterations. The normalized error is defined as,  $\left(\frac{X_{actual} - X_{iteration}}{X_{actual}}\right)$ . where *X* denotes the electron number density.

#### 4.2.2.5 Absorption path length and instrument factor

The global parameters, absorption path length,  $l_{abs}$  and instrument factor,  $F_{inst}$  affects all of the emission lines. These parameters cannot be determined simultaneously as line intensity is weakly dependent on the product of  $F_{inst}$ ,  $l_{abs}$  and  $n_i^0$ . This can be easily seen if we consider the case of an optically thin plasma, equation 3.6 where the intensity is directly proportional to the product of these three quantities. The absorption path length for a typical LIBS plasma has a value ranging from a few millimeters (in a background medium) to a few centimeters (in case of vacuum) [76]. Keeping all other parameters constant, its effect on final concentration was determined to see how much this factor influences the final estimates. The errors in final concentration estimates were not significant and will be accounted in the final values as error bars. The estimation of  $n_i^0$  could be achieved through the scheme discussed in previous section and hence it doesn't pose any challenge. The only remaining parameter is the  $F_{inst}$  which can now be obtained as a result of fitting the simulated spectrum to the experimental one.

# 4.2.3 Fitting of the synthetic spectrum to experimental spectrum

All the parameters required to generate synthetic profiles except plasma temperature, electron number density and concentration values have been discussed in the previous section. These three quantities along with the instrument factor are passed as an input parameters to generate the synthetic profiles. Using the above method, a typical synthetic profile for input plasma temperature of 12000K, and electron number density of  $5 \times 10^{16}$  cm<sup>-3</sup> for stainless steel sample having a molar concentration value of [Cr-20% Fe-70% Mn-2% Ni-8%] is generated. The same is shown in figure 4.6. A constant value of absorption path length,  $l_{abs}$  was used for generating the spectrum. The value of Lorentzian width was also taken as a constant value for all of the emission lines while generating the emission profiles. It may be noted that this value will be obtained from the experimental spectrum as explained in an earlier section once we fit these synthetic profiles on the experimental ones.

The input parameters used to generate the synthetic profiles can be obtained by performing a non-linear least square fitting of the simulated line intensities on the experimental spectrum. As explained previously, the value of true line widths from experimental spectrum requires an iterative procedure. Hence, the complete procedure requires two iterative loops and has been schematically shown in figure 4.7.

The above algorithm has been implemented in MATLAB<sup>®</sup>[54] and the fitting is automated, starting from peak identification to final concentration estimation. The iterations start with an initial temperature and electron number density value of 10000 K and  $1 \times 10^{16}$  cm<sup>-3</sup>. The concentration values are taken to be identical for all the identified elements in the experimental spectrum. These input parameter values are then adjusted



Figure 4.6: Simulated emission spectrum for stainless steel using the above method.

iteratively to match with the experimental spectrum. The complete procedure was tested on a few simulated spectrum and the fitting method resulted in perfect match with the input parameters (T,  $n_e$  and C). The computational time to analyze the complete spectrum depends on the number of emission lines and parameters to fit. For the case of steel having 4 elements and ~ 200 emission lines to fit, the method results in a total computational time of typically 20-30 min on a standard(i5 4-core) PC.



Figure 4.7: Schematic of the method used for estimating the concentration using synthetic line profiles

# **Chapter 5**

# Applications and improvements to the method

In the present chapter, some applications of the developed method (chapter 4) will be presented. The applications has been divided into two major segments, the first being retrieval of concentration from different samples and the second is predicting limit of detection for minor constituents in a multi-element sample. The detection limit has been shown to be dependent on the experimental signal-to-background ratio. One of the other application of this method could be the estimation of the accuracy expected in a CF-LIBS approach for quantitative analysis. This will be discussed later in the future work plan. Improvements to this method will be discussed at the end of this chapter.

# 5.1 Applications of the developed scheme

# 5.1.1 Quantitative estimation from multi-element sample

This section gives a brief overview of the application of the synthetic spectrum method for the concentration estimate from various samples.

#### 5.1.1.1 Brass sample

A comparatively simpler case for concentration estimation for two elements in a sample of brass was used as starting point to validate the above method. The experiments were conducted in vacuum, the details of the experimental set-up have been discussed previously. The gate width used in the experiment was 400ns with same value for acquisition delay. A total of 500 shots were averaged with the target being moved to a new position after every 20 shots.



Figure 5.1: Calibrated spectrum for brass obtained experimentally at 400ns delay after plasma initiation.

Line identification was performed using the procedure mentioned in section 2.3.3 which evaluates most intense lines for input elements at a temperature of 1eV. For the case of brass, out of a database consisting of more than 1600 lines, 56 lines were identified from the experimental spectrum and selected for analysis. The full calibrated experimental spectrum for brass is shown in figure 5.1. A simultaneous fitting was then performed on all of the identified lines to retrieve the various parameters including the concentration values. For the best fit condition shown in figure 5.2, the value of plasma temperature comes out to be,  $13200\pm700$  K and electron number density is  $2.2\pm0.9\times10^{16}$  cm<sup>-3</sup>. The concentration



Figure 5.2: A portion of simulated spectrum on the experimentally obtained LIBS spectrum for brass sample. The simulated spectrum is shown in blue and experimental spectrum is in orange color. Not all lines appearing in the above figure were used for fitting. The lines correcponding 491.1nm and 492.4nm in the experimental spectrum belong to emission from ZnII species. The atomic parameters for these lines were not available on Kurucz database and hence were not simulated.

values obtained for the brass sample using this method was compared with the EPMA measurements [77]. The values are shown in table 5.1 with an error-bar corresponding to 95% confidence interval obtained from  $\chi^2$  value of the fitting.

Table 5.1: Concentration estimates (in %) for brass sample from LIBS compared with EPMA measurements.

Elements	Cu	Zn
Present method	57.79±1.24	42.21±1.24
EPMA	59.48±0.48	40.51±0.46

#### 5.1.1.2 Steel sample

After successfully demonstrating the technique for two-element sample, it was used on a slightly complex stainless steel sample. Steel samples have been used extensively by many groups as a benchmark to compare different analytical methods based on CF-LIBS [78, 79]. The experimental condition and set-up is similar to one used for the previous sample. The steel spectrum as can be seen from the experimentally derived one (figure 5.3) is quite crowded unlike the case of brass because of many neutral and ionic Fe lines appearing in close proximity. This results in some of the lines getting merged which limits an accurate analysis. Out of more than 13000 emission lines from the database, a selection of 190 intense lines was made for analysis. The advantage of using synthetic spectrum method can be realized for such cases as it can correctly model these merged lines as well as handle a very large number of emission lines.

This can be seen clearly from the close match of simulated spectrum overlaid on the experimental spectrum shown in figure 5.4 for multiple portions of the spectrum. The final estimate of the plasma parameters obtained after fitting are, temperature value of  $10100\pm600$ K and electron number density value of  $3.1\pm1.9\times10^{16}$  cm<sup>-3</sup>. The concentration values are shown in table 5.2 along with the EPMA values for comparison.



Figure 5.3: Calibrated spectrum for steel obtained experimentally at 400ns delay after plasma initiation.

Table 5.2: Concentration estimates (in %) for steel sample from LIBS compared with EPMA measurements.

Elements	Cr	Fe	Mn	Ni
Present method	17.81±1.68	71.08±3.24	2.92±0.24	8.19±1.31
EPMA	19.64±0.29	69.62±0.51	1.77±0.22	8.96±0.33

## 5.1.1.3 Rock sample

After establishing this technique for metal samples discussed previously, it was applied on a rock sample which was present in powder form. Analysis of such geological samples have recently gained a huge impetus owing to the simplicity and suitability of the LIBS method for remote and on-site analysis [80, 81]. Although traditionally chemo-metric method of analysis have been used for such samples [82–84] where a general classification is sufficient [85, 86], the application of CF-LIBS method for quantitative analysis has been also quite popular [20, 87].

This experiment was conducted in air. Pellets were formed from the powdered and



Figure 5.4: Multiple portions of simulated spectrum overlaid on the experimentally obtained LIBS spectrum for steel sample. The simulated spectrum is shown in blue and experimental spectrum is in orange color.

dried sample using 150 kN hydraulic press. XRF measurements were also carried out on the sample to compare it with LIBS, pellet preparation for which was similar except for the use of wax binder in case of XRF samples. The acquisition delay used in this experiment was 2.5  $\mu$ sec and a gate width of 2.0  $\mu$ sec. A total of eight elements could be identified in the spectrum with more than 120 emission lines used for the analysis. The number of fitting parameters in this case is evidently quite large compared to the previous cases and hence, the computational time on single core processing was considerably high. Hence, all of the MATLAB<sup>®</sup> routines involving iterative steps were rewritten to make use of the multi-core processing for parallel computation. This considerably reduced the computational time for the fitting routines.



Figure 5.5: Simulated spectrum along with the experimentally obtained LIBS spectrum for rock sample

The matching of the synthetic spectrum on the experimental spectrum is shown in figure 5.5. The resultant value of plasma parameters along with the concentration value is given in table 5.3. Values from XRF measurements are also mentioned in the table. Since XRF measurements provides the weight concentration values in element oxide form, the molar

concentration of elements from LIBS are converted to weight fractions in oxide form using stoichiometric coefficients for respective elements [88]. While the result shows reasonable agreement for most of the oxides,  $Fe_2O_3$  and MnO do not show a proper match with the XRF values. This is mainly attributed to the overlapping of multiple lines in the vicinity for these two elements resulting in inaccurate estimation of peak line intensity. Moreover, since there is a normalisation of the concentration involved in LIBS analysis, the error in minor constituents may appear enhanced when compared with major elements.

Table 5.3: Concentration estimates (in %) for rock sample from LIBS compared with XF	۲F
measurements.	

Element oxide	Present method (LIBS)	XRF
	$T = 9788 \pm 332 \text{ K}$	
	$n_e = 5.32 \pm 2.16 \times 10^{16} \mathrm{cm}^{-3}$	
$Al_2O_3$	7.06±1.49	7.97±0.04
CaO	2.13±0.48	2.77±0.01
$Fe_2O_3$	12.89±1.42	$6.55{\pm}0.05$
MgO	1.18±0.22	2.98±0.32
MnO	6.93±0.91	2.88±0.01
Na <sub>2</sub> O	$1.08 {\pm} 0.74$	$1.44{\pm}0.06$
SiO <sub>2</sub>	68.32±5.25	70.87±0.15
TiO <sub>2</sub>	0.41±0.28	0.39±0.01

#### 5.1.1.4 Accuracy in concentration estimate

Although results obtained by applying this method to different samples presented in the previous subsections show much better estimates for major elements, the concentration estimate for minor constituents using CF-LIBS have considerably larger errors. This is inherent to the CF-LIBS approach and the three major contributing factors for this are discussed below. The first factor which contributes to this error is the uncertainties associated

with the atomic parameters used for fitting the experimental spectrum. The second factor is the assumptions (plasma homogeneity and stoichiometric ablation) which we make to derive an LTE spectrum as discussed in section 1.5. While the above two factors affect the concentration estimate for all elements (major and minor), a relatively larger uncertainty in the concentration estimate of minor constituents is mostly due to last and probably the most important factor which is the normalization of the concentrations in the CF-LIBS method. The CF-LIBS procedure inherently requires all concentrations to be normalized which results in adding of all uncertainties thereby the minor constituent's estimation goes off by a larger extent when compared with a major element in the same sample. The effect of these three factors on the concentration estimate can be studied by the synthetic spectrum method presented in the thesis, a plan for which has been explained in chapter 7 discussing future works.

## 5.1.2 Predicting detection limits in multi-element samples

It may happen that the emission intensity for minor elements in a multi-element sample may fall below the experimental signal-to-background ratio (SBR). In such cases, those elements remain undetected in the LIBS technique. Hence, by utilizing the synthetic spectrum generation method, a scheme is developed to predict the detection limit for elements based on the signal to background ratio.



Figure 5.6: Variation of experimental SBR with acquisition delay



Figure 5.7: Simulated line intensity ratio of the most intense line of neutral silicon and potassium/phosphorous species at the experimentally determined temperature and electron number density. Also shown is the experimental value of SBR from figure 5.6.

This work is motivated by the fact when we conducted XRF on the rock sample, the XRF results also showed presence of potassium and phosphorous in the sample which were missing in the LIBS spectrum. To understand the non-appearance of emission lines corresponding to these two elements, simulated spectrum to obtain emission line intensities for the most prominent line for Si, K and P were obtained at different concentrations at experimental value of plasma conditions (of T and  $n_e$ ). It was then proposed that, detection limits for these elements at the experimental SBR is the reason why these elements are not seen in the spectrum. The value of SBR was obtained experimentally as a function of acquisition delay and is shown in figure 5.6.

To verify this conjecture, ratio of the most intense line of the minor elements (K and P) to the major element (Si) was obtained as a function of concentration of those elements (K and P) at temperature and electron number density mentioned in table 5.3. Available literature suggests a trend of the line intensities as shown in the figure 5.7 obtained through simulation. The experimental SBR is also shown in the plot for comparison.

From figure 5.7, it is clear that the detection limit (of the experimental system) for potassium in the sample is 4% and hence is not visible in the recorded spectrum. Similar analysis can be carried out for different elements and hence, a predictive capability can be built into the algorithm if the experimental SBR is known for the system.

# **5.2** Improvements to the developed scheme

The synthetic spectrum method has been successful in deriving concentration from various multi-element samples with reasonable accuracy as demonstrated in the present chapter. Still, it suffers from some limitations which is one of the reasons for the error-bars appearing in results shown in table 5.1, 5.2 and 5.3. These are discussed in the next sub-sections.

## 5.2.1 Plasma inhomogeneity

One of the assumptions made while constructing the radiative transfer equation for thick plasma was of plasma homogeneity. This implies that the plasma length along the line of sight of recording is assumed to be at a single value of temperature and electron number density. Although this condition is met because of the homogenization of the plasma due to electron re-collisions in the initial phases of plume evolution, there have been some reports using spatially resolved spectroscopy regarding inhomogeneity in plasma behavior for certain acquisition delay-gate settings [46, 88]. It has been shown that the emission of ionic species is mostly from the central portion of the plasma, which is supposedly at a higher temperature compared to emission from neutral species which are predominantly from the periphery [46]. In such cases, single plasma temperature may not give a correct picture of the emissions from the plasma and one has to take into account the spatial inhomogeneity. This aspect will be covered briefly once again in the plan for future work where a discussion on multi-layer model of plasma is presented.

# 5.2.2 Stark broadening parameters

The estimation of true line widths from the experimental spectrum through iterative procedure explained in section 4.2.2.2 provides only an approximate measure of this quantity. This is mostly because of the fact that the values are obtained from a multi-parameter iterations involving co-dependent parameters. The only correct way to estimate true Lorentzian widths is its computation through Stark broadening parameters as the profiles are mostly Stark broadened. Given the paucity of Stark broadening parameters in literature for most of the transitions, we face a hurdle in our quantitative analysis. Also, theoretical calculations of these parameters for different electronic transitions of various elements are complex. Moreover, it has been observed that the theoretical values, shows considerable disagreement with the experimentally derived values of the Stark parameters.

Hence, there is a need to obtain these parameters experimentally for various transitions for elements to be used in LIBS. A method to obtain these broadening parameters is a topic of discussion in the next chapter.

# **Chapter 6**

# **Determination of Stark parameters**

As presented in the last chapter, spectral lines observed in a typical LIBS experiment are influenced by various atomic parameters of the transition such as oscillator strengths, partition functions, statistical weights and energy of the levels involved. Apart from these parameters which are easily accessible from available atomic databases [65, 66], another parameter which governs the emission line widths is the Stark broadening parameter. The value of this parameter is not readily available for many transitions for typical values of plasma parameters in LIBS experiments. The theoretical calculation for Stark parameters have been performed mostly by Griem [89] and others [90] for selected transitions of different elements. Most of the early experimental determination through optical measurements assume plasma to be optically thin [91–93]. The estimation of the Stark parameters through LIBS measurements has been reported lately for both optically thick and thin plasma conditions [47, 52, 94, 95]. A detailed study on various experimental factors affecting these measurements in typical LIBS experiment can be found in [52].

The issue with experimental determination of broadening parameter for thick plasma is convoluted broadening due to self-absorption in the plasma. The self-absorption broadening in turn depends on the intrinsic broadening due to Stark effect as shown in figure 6.1. It can be clearly seen from the figure that the observed line width (FWHM) has a strong dependence on the Stark width of the line. Hence, non-availability or ambiguous value of Stark broadening parameters compels one to exclude many lines, though intense, from the analysis. This results in error in the estimated value of plasma parameters, viz., temperature, electron number density and final concentrations. It's effect on temporal evolution of electron number density for Aluminum plasma has been demonstrated by Surmick and Parigger [96].



Figure 6.1: Simulated profiles demonstrating line broadening (shown by arrows) due to self absorption at different values of Stark width ( $\Delta\lambda_{Stark}$ ) keeping all other parameters same. The observed widths for both the cases are also shown. The intensities are normalized to a common maximum value.

The present chapter mainly deals with the determination of these parameters experimentally so as to utilize them in the quantitative analysis using LIBS. A method utilizing time resolved LIBS measurements will be explored and its efficacy demonstrated for a simple case of neutral Aluminum lines.

# 6.1 Stark effect in laser plasma

The emitters in the plasma are embedded in a local electric field due to fast moving electrons and relatively slower ions in their vicinity. The field results in a perturbing force acting on the emitting species, which experiences Stark effect. As a result, the energy levels of the perturbed system undergo splitting and shifting. The perturbing electric field,  $\varepsilon$ , experienced by an atom in the vicinity of a charge 'q' (due to ions or electrons) can be easily written as,

$$\varepsilon = \frac{q}{4\pi\varepsilon_0 r^2} \tag{6.1}$$

For hydrogen and hydrogen like atoms, the energy shift is proportional to this perturbing electric field ( $\Delta E_{shift} \propto \varepsilon$ ) that is, the linear Stark effect [30]. The energy levels involved in this case undergo similar shifts and as a result, broadening of the emission line is symmetric about the central transition wavelength and shows no shift. In this case, the electron number density in the plasma can be related to the line width as [89]

$$n_e = C(n_e, T, \lambda) \Delta \lambda_{FWHM}^{\frac{3}{2}}$$
(6.2)

The term C in the above equation can be treated as constant in analysis for a given transition as it shows a weak dependence on the temperature and electron number density. A much more accurate expression for typical plasma conditions in LIBS has been obtained by Cvejic et al. [93] and will be used in the present chapter for all analysis. It is given as,

$$n_e = 10^{17} \times \left(\frac{\Delta \lambda_{FWHM}}{1.098}\right)^{1.47135} \tag{6.3}$$

The value of  $n_e$  and  $\Delta \lambda_{FWHM}$  in the above equation are to be put in units of  $cm^{-3}$  and nm respectively.

The shifts in the energy levels for all other atoms predominantly show quadratic Stark effect which is described by second order perturbation theory. The splitting of the individual energy levels in this case is asymmetric resulting in an asymmetric broadening of the line, with an overall shift in the central wavelength (which appears red-shifted). In such cases, the line width is related to the electron number density through the following expression [9, 23],

$$\Delta\lambda_{FWHM} = 2w_s(T, n_e) \frac{n_e}{10^{16}} \left[ 1 + 1.75 \times 10^{-4} A(T, n_e) n_e^{\frac{1}{4}} \left( 1 - \frac{3}{4} n_D^{-\frac{1}{3}} \right) \right]$$
(6.4)

where,  $w_s$  and A are the electron and ion broadening Stark width parameters respectively depending very weakly on the plasma temperature and electron number density. This dependence will be ignored throughout the analysis presented later in this chapter.  $n_D$  represents the number of particles in the Debye sphere and is given by,

$$n_D = 17.2 \times \left(\frac{10^{16}}{n_e} T^3\right)^{\frac{1}{2}}$$
(6.5)

The resultant shift in the transition wavelength because of the unsymmetrical energy level shifts in this case can be expressed as [9, 23],

$$\delta\lambda = \frac{n_e}{10^{16}} \left[ d_s(T, n_e) \pm 2.0 \times 10^{-4} A(T, n_e) w_s(T, n_e) n_e^{\frac{1}{4}} \left( 1 - \frac{3}{4} n_D^{-\frac{1}{3}} \right) \right]$$
(6.6)

where,  $d_s$  is the Stark shift parameter having a weak dependence on both temperature and electron number density which is ignored for the present analysis.

# 6.2 Methodology

The method to obtain the Stark parameters from self absorbed lines observed experimentally relies on correct determination and removal of the self absorption broadening from the total line width. There have been different approaches in the literature to do this. Notable among them is the use of duplicating mirrors by Moon et al. [94] and by exploiting the relation between line parameters (peak intensity, width, integrated intensity) and the plasma opacity values obtained by Ammamou et al. [97]. While the former requires extra experimental arrangements, the latter approach uses the observed widths and line intensity to correct for the self absorption effects. The later approach has been used by many groups to evaluate self absorption in quantitative elemental analysis [72, 88, 98, 99]. While all of the above work assumes plasma to be in LTE, Liu et al. [100] have used a cross-calibration method in multi-element sample which does not rely on the LTE assumption.

Following the work by Ammamou et al. [97], a method utilizing the time resolved LIBS measurements to determine Stark parameters will be discussed in this section. A brief overview of line parameter dependence on optical thickness of the plasma will be presented first followed by a scheme to use time resolved measurements to compute these broadening parameters.

# 6.2.1 Relation between peak intensity and line width

The value of absorption coefficient, or opacity term given in equation 4.2 can be simplified if only Lorentzian component of the line width is considered. This is possible because as explained in section 4.2.2.1, the Doppler broadening in a typical LIBS plasma can be safely ignored. In that case, the opacity term considering only Lorentzian width can be written as [61, 97, 101],

$$\kappa_{\lambda}^{ji} = \frac{2e^2g_if_{ij}n_0\lambda^2}{mc^2U(T)} \left(\frac{\Delta\lambda_L}{4(\lambda-\lambda_0)^2 + \Delta\lambda_L^2}\right) \exp\left(-\frac{E_i}{k_BT}\right)$$
(6.7)

Moreover from equations, 3.1, 3.2, 3.6 and 4.3, the relation between line intensity for optically thin and thick cases be written as,

$$\frac{I_{\lambda}}{I_{\lambda}^{\dagger}} = \frac{1 - \exp(-\tau_{\lambda})}{\tau_{\lambda}}$$
(6.8)

where  $\tau_{\lambda}$  is optical depth given by,

$$\tau_{\lambda} = \kappa_{\lambda}^{ji} \times l_{abs} \tag{6.9}$$

Using the above two equations, relation between various characteristics of the line (peak intensity,  $I_{\lambda=\lambda_0} = I_0$  and line width) for optically thin and thick cases can be derived as follows [97],

$$\frac{I_0}{I_0^{\dagger}} = \frac{1 - \exp(-\tau_0)}{\tau_0} \tag{6.10}$$

and

$$\frac{\Delta\lambda_0}{\Delta\lambda_0^{\dagger}} = \left[-1 - \frac{\tau_0}{\log(1 + \frac{\exp(-\tau_0)}{2})}\right]^{\frac{1}{2}}$$
(6.11)

The above two ratios can be numerically computed at different values of optical thickness  $\tau_0$  and the same is shown in figure 6.2. From these values, the ratios can then be used to relate the peak line intensity values with line width parameters. This is shown in figure 6.3 which exhibits a smooth variation of the two parameters. Hence, to relate these two parameters, a function of the form  $y = a \times x^m$  is fitted on to the data points. The value of coefficients, *a* and *m* obtained for the best fit condition are, a = 0.9822 and m = -1.753.

Hence the relation between these two ratio can be written as,



$$\frac{I_0}{I_0^{\dagger}} = 0.9822 \left(\frac{\Delta\lambda}{\Delta\lambda^{\dagger}}\right)^{-1.753}$$
(6.12)

Figure 6.2: Peak line intensity ratio and line width ratio computed at different values of optical thickness.

The value of these coefficients result in fitting error always less than 1%. By using only power law type dependence with similar exponent values, Sherbini et al. [98, 102] have computed self absorption in a few lines of Aluminum while the same method has been used by Praher et al. [88] in quantitative estimation of metal oxides. The present scheme also utilizes this relation to estimate the Stark broadening parameters which is discussed in the next section.

# 6.2.2 Time resolved measurements to compute Stark width parameter

The equation 6.12 can be rearranged so as to bring all optically thick parameters on one side and optically thin on another side,



Figure 6.3: Relation between peak intensity ratio and line width ratio obtained from values shown in figure 6.2.

$$I_0[\Delta\lambda]^{1.753} = 0.9822 \times I_0^{\dagger}[\Delta\lambda^{\dagger}]^{1.753}$$
(6.13)

The advantage of this manipulation lies in the identification of the LHS of equation 6.13 with experimentally observed quantities which are peak line intensity and line width of the self absorbed line. The RHS of the equation includes terms which are to be computed assuming optically thin plasma. In this, the value of peak line intensity can be obtained once we have the value of plasma temperature and line width is only due to Stark broadening whose dependence on electron number density has been shown in equation 6.4. Hence, if the value of plasma temperature and electron number density is known, the two terms can easily be compared to retrieve the Stark width parameter  $w_s$  from equation 6.4.

For a pair of lines, the equation 6.13 can be written as,

$$\underbrace{\frac{I_0}{I_0^{ref}} \left[\frac{\Delta\lambda}{\Delta\lambda^{ref}}\right]^{1.753}}_{Y_{obs}} = \underbrace{\frac{I_0^{\dagger}}{I_0^{\dagger ref}} \left[\frac{w_s}{w_s^{ref}}\right]^{1.753}}_{Y_{cal}}$$
(6.14)

The term on the left hand side, marked as  $Y_{obs}$  can be obtained experimentally at different plasma evolution times having different opacity values. For  $\Delta\lambda$ , equation 6.4, the calculation requires electron number density which can be obtained using Stark broadening of the  $H_{\alpha}$  line present in the spectrum using equation 6.3. It may be noted that the contribution of the broadening due to ion impact is very small compared to electrons at typical values of plasma temperature and electron number density observed in LIBS. The contribution due to ion broadening comes out to be less than 4% of the electron broadening [50] and hence only electron impact broadening is considered. In such cases, a linear expression relating electron number density and line width can be established as [47, 93, 103, 104],

$$\Delta \lambda^{\dagger}(t) = 2w_s \frac{n_e(t)}{10^{16}} \tag{6.15}$$

where  $n_e(t)$  is obtained using equation 6.3 as,

$$n_e(t) = 10^{17} \times \left(\frac{\Delta \lambda_{H_\alpha}(t)}{1.098}\right)^{1.47135}$$
(6.16)

The calculation of line intensity term requires value of temperature which can be obtained along with the Stark width parameter. By taking a ratio, other unknown parameters required for line intensity calculation,  $F_{inst}$  and  $l_{abs}$  have been eliminated. Hence, the two terms can be compared at different times and the resultant error can be expressed as,

$$\varepsilon = Y_{obs}(t, \lambda_0) - Y_{cal}(T(t), n_e(t), w_s(\lambda_0))$$
(6.17)

Hence, to obtain the Stark width parameters,  $w_s$  and the temperature value, T(t), the task is to minimize the above error,  $\varepsilon$ . The value of temperature varies with the time, while  $w_s$  is constant for any transition. By performing multi-parameter iteration on the temporal data, the value of plasma temperature T(t) and Stark width parameters,  $w_s$  can be estimated.

The above situation is simplified further if the lines used in denominator of equation 6.14 belong to the same species as in numerator and have identical or very similar values

of upper state energy level and transition wavelength. In such cases, by using equation 6.7, a further simplification to equation 6.14 can be obtained as,

$$\frac{I_0}{I_0^{ref}} \left(\frac{\Delta\lambda}{\Delta\lambda^{ref}}\right)^{1.753} = \frac{F_{\lambda}^{inst}}{F_{\lambda^{ref}}^{inst}} \frac{gf}{g^{ref} f^{ref}} \left(\frac{w_s}{w_s^{ref}}\right)^{0.753}$$
(6.18)

As can be seen from the above equation, the terms on the right side are independent of temperature and hence, a direct estimate of the Stark broadening parameters is possible just by comparing the experimentally observed ratio of line intensity and width.

## 6.2.3 Time resolved measurements to compute Stark shift parameter

The estimation of Stark shift parameter from time resolved measurements is straightforward once electron number density,  $n_e(t)$  is obtained for different acquisition times. This is possible by use of equation 6.6 in which the contribution of ion impact parameter to the shifts can be safely neglected. In such a case, the wavelength shifts can be expressed as [93, 104],

$$\delta\lambda(t) = d_s \frac{n_e(t)[in\ cm^{-3}]}{10^{16}} \tag{6.19}$$

From the slope of a straight line fit to the plot of observed shifts  $\delta\lambda(t)$  as a function of electron number density values,  $n_e(t)$ , value of Stark shift parameter  $d_s$  can be obtained as shown later in figure 6.8.

# 6.3 Implementation and verification of the developed methodology

The verification of the developed scheme was performed on simulated data assuming a functional form for  $n_e(t)$  and T(t) and  $w_s$  for some transitions. The simulated profiles were drawn at the actual instrument resolution used for the experiment later on. The method discussed in the chapter 4 has been used to generate the synthetic profiles at different times. Figure 6.4 shows one such case for a temperature value of 14000K and electron number density value of  $1 \times 10^{18} cm^{-3}$  for two Aluminum lines. The lines are merged because of large self absorption broadening. The analysis step involves first determination

of the observed Lorentzian line width of the emission line profile using the numerical deconvolution of the experimental spectrum. For this, the value of spectrometer resolution as calculated using Hg-Ar lamp, discussed in section 2.2.3 is used. Since, the nearby lines may get merged at high degree of self-absorption, a simultaneous fitting of the line was performed to obtain the peak intensity value and the observed line widths for each transition wavelength. These experimentally observed values are then compared with the thin plasma values which is changed iteratively so as to minimize the error mentioned in the previous section.

The method was tested on simulated data, by using multiple Voigt profiles to fit as shown in figure 6.4. Al II emission line at 281.6 nm was used as reference for which the Stark parameters were already known from existing literature [105]. The profile matches perfectly and the value obtained for plasma temperature and Stark width parameters using an iterative error minimization procedure results in a perfect match with the input values used for simulations.

After verifying its performance on simulated data, it was also validated on experimentally observed data. This is discussed in the next subsections.

# 6.3.1 Experimental scheme

The experimental set-up is similar to what was used for the work presented in previous chapter (chapter 4). Aluminum was used as a target and the spectrum recorded between  $0.5\mu sec$  to  $10\mu sec$  in steps of 500ns with same value of gate width. Spectrum recorded at different timescales of plasma evolution and hence opacity showed different degrees of self absorption. Two such contrasting cases are shown in figure 6.5.

# 6.3.2 Evaluation of Stark parameters for neutral Al lines

The evaluation of the Stark parameters follows the general prescription described earlier in this chapter. As mentioned previously, as a first step, electron number density from  $H_{\alpha}$ line and line widths (Lorentzian component after de-convolution) for various Aluminum lines through multiple Voigt profile fit were obtained as a function of time. This is shown



Figure 6.4: Simulated profile for a few lines of Aluminum showing merging of nearby lines due to self absorption. Also shown is the efficacy of the fitting routine to correctly obtain the value of peak intensity and line width.

in figure 6.6 for one of the Aluminum lines ( $\Delta\lambda_0 = 394.4 \text{ } nm$ ). Note that the time value on the X-axis is not centered at the ICCD gate.

#### 6.3.2.1 Stark width parameter

The Stark width parameter of the Aluminum lines were obtained by obtaining values of  $Y_{obs}$  at different times and comparing it with calculated value of  $Y_{cal}$  using equation 6.14. Starting from an initial guess value for T(t) and  $w_s$  for different lines, the value of  $Y_{cal}$  was adjusted until a best match is found. Since the value of observed line width falls below the instrument resolution for large delays (figure 6.6), data only up to  $3\mu sec$  have been used in this analysis. The value of plasma temperature T(t),  $Y_{obs}$  and  $Y_{cal}$  for best fit conditions for two of the lines are shown in figure 6.7.

Based on the final iteration, the value of Stark width parameter obtained for the set of emission lines is shown in table 6.1 along with a comparison with existing values, both



Figure 6.5: Experimental line profile for two lines of Aluminum at different times (0.5 $\mu$  sec - top and 5 $\mu$  sec - bottom) having different values of opacity and self absorption. The ionic line of Aluminum (281.6nm) used as reference and  $H_{\alpha}$  line (656.28nm) used for electron number density calculation can also be seen in the figure.

theoretical and experimental, available in literature.

## 6.3.2.2 Stark shift parameter

The Stark shift parameters for different Aluminum lines are obtained using equation 6.19. A plot of observed line shifts vs.  $n_e$  is shown in figure 6.8 for two of the neutral lines. It may be noted that the values of observed shifts are used only up to a time delay at which its value is greater than the expected accuracy of wavelength calibration of the spectrometer. Slope of the straight line fit in figure 6.8 gives the value of Stark shift parameters which are


Figure 6.6: Electron number density and line width (for  $\Delta\lambda_0 = 394.4 \text{ nm}$ ) along with the error bars obtained as a function of acquisition delay.

listed in table 6.2 along with the values available in literature.

As seen from tables 6.1 and 6.2, the values of Stark parameters obtained using multitime observation data shows promising result. The method can be certainly extended to other transitions in different elements.



Figure 6.7: Value of T(t),  $Y_{obs}$  and  $Y_{cal}$  for the best fit condition. The Stark width parameters are obtained from the  $Y_{cal}$  values shown in this plot.

Table 6.1: Values of stark width parameter,  $w_s$  obtained for four resonant lines of Al I. Also shown are the theoretically calculated and experimental values available in the literature. The theoretical values (denoted with exponent 'c') are obtained from reference [90] while experimental values (denoted with exponent 'e') are obtained from reference [106]

Wavelength(nm)	<i>w</i> <sub>s</sub> (in nm)	<i>w<sub>s</sub></i> (in nm)	
	Present work	Literature	
308.21	$0.0029 {\pm} 0.0008$	$0.0043^c, 0.0045^e$	
309.27	$0.0037 {\pm} 0.0011$	$0.0043^c, 0.0049^e$	
394.40	$0.0021 \pm 0.0006$	$0.0029^c, 0.0037^e$	
396.15	$0.0024{\pm}0.0007$	$0.0029^c, 0.0038^e$	



Figure 6.8: Wavelength shifts as a function of electron number density. Also shown is a straight line fit to the data points for estimation of Stark shifts.

Table 6.2: Values of Stark shift parameter,  $d_s$  obtained for four resonant lines of Al I. Also shown are the theoretically calculated and experimental values available in the literature. The theoretical values (denoted with exponent 'c') are obtained from reference [90] while experimental values (denoted with exponent 'e') are obtained from reference [107]

Wavelength(nm)	$d_s(\text{in nm})$	$d_s(\text{in nm})$	
	Present work	Literature	
308.21	$0.0014 {\pm} 0.0004$	$0.0015^e, 0.0020^c$	
309.27	$0.0014 {\pm} 0.0004$	$0.0015^e, 0.0020^c$	
394.40	$0.0022 \pm 0.0004$	$0.0024^e, 0.0023^c$	
396.15	$0.0024 \pm 0.0005$	$0.0024^e, 0.0023^c$	

### Chapter 7

### **Conclusion and future directions**

### 7.1 Conclusion

Quantitative analysis using the CF-LIBS procedure is a promising area of research given its simplicity and wide applicability. Under the assumption of an homogeneous and stoichiometric LTE plasma, the concentration of various species in the plasma can be mapped with the intensity values. An effort to correctly formulate this relation, utilising the radiative transfer equation for different plasma opacity, has been made in the present thesis. Starting with the case of an optically thin plasma, a ratio based procedure to retrieve quantitative information has been presented. The method has been compared with conventional methods of CF-LIBS analysis for its accuracy and ease of implementation. The use of neutral number density ratios eliminates the contribution of the instrument factor in the analysis steps. Moreover, it limits the number of parameters which require tuning to get the final estimates.

Advancing from the above, the requirement of plasma to be optically thin has been relaxed by the use of synthetic spectrum method. This particular development is the main highlight of the present thesis. Self absorption in the plasma is correctly accounted while generating simulated profiles which are later fitted on to the experimental spectrum. Synthetic emission profiles have advantage in terms of their usefulness in analysis of dense spectrum with merged lines whose analysis is otherwise difficult. All plasma parameters are obtained as a result of this multi-parameter fitting. The simultaneous fitting of a large number of lines reduces the error in estimation of the concentrations. Automatic line identification algorithm based on evaluating most significant lines at typical LIBS plasma temperature, developed in this context, is a particularly important step towards improvement of the analysis procedure. This will help in reducing human error when analyzing complex spectra. In the course of development of necessary routines for implementation of synthetic spectrum method, parallel processing method to reduce the computational time has also been attempted. This has proved helpful in cases involving samples having hundreds of emission lines from large numbers of elements.

The limits of the CF-LIBS method is currently being expanded to include more number of elements in the analysis. Hence, one of the important application of the developed method which becomes relevant in the current time is the ability to predict the detection limit of various elements for an experimental system. Based on the temporal evolution of the SBR, detection limit for minor constituents in a sample can be estimated by comparing most intense simulated line for a minor element to a major element at the given experimental conditions. This has been successfully used to explain non-appearance of the emission signature in LIBS for some of the elements in a particular sample. The analysis is also important from point of view of designing the experiment. The acquisition time can be optimized for a particular species to have it best shot at getting detected.

One of the limitations of the developed method is the need of Stark parameters for line under study which are seldom available. Hence, a study into experimental determination of Stark parameters have been performed. A technique utilising time resolved data to correctly estimate broadening parameters have been demonstrated. The use of time resolved data increases the number of data points while maintaining the number of parameters to be fitted. The intricate dependence of the line broadening due to self absorption and Stark broadening is correctly modeled utilising the relation between the emission line parameters and the opacity of the plasma. In this connection, an expression relating the observed line width and the Stark broadening parameter have been derived for the condition when the two emission lines under study belong to the same species and have nearby upper state energy levels. The expression obtained is independent of the temperature and purely depends on the emission line parameter and hence can be used as a testing standard since it is less prone to error.

Thus, the main objective of the present thesis to develop methodology to correctly account for self absorption in optically thick plasma has been achieved. Through appropriate improvements and additions to the analysis technique, the work presented in thesis will help in making the CF-LIBS method more versatile. Extension of the developed methodology along with some other improvements is planned as a future work which will be discussed in the next section.

### 7.2 Future directions

#### 7.2.1 Relaxation of plasma homogeneity condition

The synthetic spectrum technique demonstrated in chapter 4 for determination of elemental composition assumes a homogeneous plasma defined by a single value of temperature and electron number density. Although this assumption is valid for ablation with fundamental wavelength of Nd:YAG, it has been observed that with KrF excimer laser having similar laser fluence there is a splitting in the peak for major emission lines, figure 7.1. This may



Figure 7.1: Peak splitting observed in one of the resonant Al I emission lines when excimer laser is used for ablation.

be a signature of in-homogeneous plasma and for such cases it is essential that a multi-layer model be constructed to truly explain the spectral signature [46].

#### 7.2.2 Nano-particles enhanced LIBS

As discussed in the chapter 5, detection limits are dependent on the experimental SBR. Hence, one of the methods to improve upon the detection limit is to improve the LIBS signal from the plasma. There have been recent reports of enhancements in line intensities using nano-particles(NP) on the surface of LIBS target [108–112]. Although a complete understanding for this enhancement is still being investigated, it is believed to be a result of improvement in ablation efficiency because of reduced thermal conductivity due to nano-particles [6]. In addition, use of nano-particles result in enhancement of the local electric field by 2-3 orders of magnitude resulting in generation of seed electrons which further absorbs and excites the plasma [109, 110].

Some preliminary experiments in NE-LIBS were conducted to observe signal enhancements and to verify improvements in SBR. Aluminum NP was spin coated on a brass target at different concentration of NP. Enhancement in emission signals have been observed for different species in the plasma [113]. The enhancement as a function of Al NP is shown in figure 7.2.

A detailed study in this area will be undertaken in near future to understand the underlying mechanism of these enhancements and to characterize the plasma formed during NE-LIBS.

#### 7.2.3 Limit of detection

A more detailed study to understand the effect of acquisition delay (and hence SBR) on the limit of detection(LOD) of various elements in LIBS was undertaken recently. This was motivated by the work presented in chapter 4. The task involved two steps, first is to generate simulated calibration curves for minor elements at different values of electron number density and temperature. Since the laser plasma is evolving with time, the values of the individual number density of elemental species and plasma temperature changes with



Figure 7.2: Signal enhancements in a few lines at three different concentrations of Al nanoparticles on a brass target

time. Hence the second step involves finding out the temporal evolution of these plasma parameters.

The first part has been completed and the result for one of the species is shown in figure 7.3. The second part requires systematic experiments on different samples at different acquisition delays. The data from those experiments will be used to obtain temporal evolution of SBR and plasma parameters. Based on the obtained values, we can then predict limit of detection of various elements under different experimental conditions. The method can also be used to optimise experimental parameters to enhance the LOD for minor elements. The work on these aspects are currently under progress.

#### 7.2.4 Stark broadening parameter database

As mentioned in chapter 6, by utilising the time resolved LIBS data, we have obtained Stark broadening parameters for a few resonant Al I lines. In those experiments, full temporal data could not be utilised because the Stark broadening quickly falls below the spectral



Figure 7.3: Variation of emission line intensities for intense line of PI as a function of temperature and electron number density.

resolution of the spectrometer for larger time delays. Hence, it is planned to utilize newly installed 0.75m Czerny-Turner spectrograph to further expand these studies. Moreover, to better constrain the plasma length value used in the calculation of simulated line intensities, a simultaneous imaging of the plasma is also proposed.

#### 7.2.5 Estimation of accuracy in concentration using CF-LIBS

One of the advantages of the synthetic spectrum method discussed in chapter 4 is that the effect of varying atomic parameters on the resultant spectrum for different elements can be studied easily. This offers an interesting perspective that the method can be used to perform a numerical study of error propagation due to uncertainty in various atomic parameters (eg., partition functions, oscillator strengths, etc.). Hence, a realistic limit of error bounds on the value of final parameters estimated using LIBS can be predicted for various samples.

### 7.2.6 Plasma spectroscopy using fs-laser

With the new femto-laser recently installed in our group, extension of the previous studies with this laser will be attempted. The shorter time scale of excitation results in partial atomisation of the plasma constituents and opens a new area of investigation of molecular signatures (band spectrum) along with atomic lines. The basic assumptions of plasma homogeneity, local thermodynamic equilibrium and stoichiometric ablation in a calibration free LIBS will be verified for such situations. The applicability of the techniques developed for nanosecond laser ablation will be tested for the new system.

Appendix A

**Emission lines used in the analysis** 

# A.1 List of emission lines along with atomic parameters used for analysis of brass sample using ratio based algorithm

Sr.No.	Wavelength(nm)	Species	log(gf)*	$E_k(cm^{-1})^*$
1	406.2637	Cu I	- 0.506	55391.29
2	427.5103	Cu I	- 0.157	62403.32
3	437.8146	Cu I	- 0.643	62948.29
4	448.0345	Cu I	- 1.743	52848.75
5	450.9369	Cu I	- 0.744	64472.3
6	453.0781	Cu I	- 1.250	52848.75
7	453.9708	Cu I	- 0.501	63584.57
8	458.6953	Cu I	- 0.313	62948.29
9	465.1119	Cu I	0.037	62403.32
10	468.0134	Zn I	- 0.815	53672.28
11	472.2153	Zn I	- 0.338	53672.28
12	481.0528	Zn I	- 0.137	53672.28
13	491.7892	Cu II	0.815	138075.6
14	493.1698	Cu II	0.915	135933.9
15	495.3724	Cu II	0.918	138064.3
16	501.6629	Cu I	- 0.913	64472.3
17	505.1793	Cu II	0.827	136160.6
18	507.6125	Cu I	- 0.748	64657.8
19	508.8277	Cu II	0.488	136035.3
20	510.5537	Cu I	- 1.516	30783.69
21	515.323	Cu I	0.217	49935.2
22	521.8197	Cu I	0.476	49942.06
23	529.251	Cu I	- 0.436	62403.32
24	539.1656	Cu I	- 0.867	62948.29
25	570.0237	Cu I	- 2.312	30783.69
26	578.2127	Cu I	- 1.720	30535.3
27	636.3338	Zn I	0.15	62458.56

\*g: statistical weight of the level involved in transition, f: oscillator strength of the transition,  $E_k$ : Upper state energy level of the

transition

## A.2 List of emission lines used for analysis of steel and brass samples using synthetic spectrum method

Cu I	324.31	327.39	327.98	329.05	330.79	331.72
	331.96	333.78	334.92	336.53	341.4	347.6
	351.18	352.42	352.74	353.38	368.74	402.26
	406.26	427.51	437.81	450.93	453.08	453.97
	458.69	465.11	467.48	470.45	510.55	515.32
	521.82	522.01	529.25	578.21		
Cu II	490.97	491.79	493.16	493.72	495.16	495.37
	500.68	502.12	504.73	505.18	506.54	506.7
	508.82	621.69	627.33			
Zn I	328.23	330.26	334.5	468.01	472.22	481.05
	636.23					

Table A.1: Brass (Cu, Zn) sample, the wavelength values are expressed in nm

Table A.2: Steel (Fe, Cr, Mn, Ni) sample, the wavelength values are expressed in nm

Fe I	300.09	300.81	300.96	302.58	303.74	304.76
	305.9	306.72	307.57	319.69	320.04	321.16
	321.96	322.58	323.94	328.67	330.6	340.75
	342.71	344.06	346.58	347.54	349.06	353.66
	354.1	354.2	355.5	355.85	356.54	357.02
	358.12	358.53	358.61	358.7	360.54	360.67
	360.88	361.02	361.88	362.14	363.14	364.04
	365.14	368.74	370.92	371.99	372.76	373.48
	373.71	374.34	374.56	374.82	374.94	375.82
	376.38	376.56	376.72	379.5	381.58	382.04
	382.12	382.58	382.78	383.42	384.04	384.1
	385.99	388.62	390.29	396.92	404.58	406.35
	407.17	414.38	426.04	427.17	430.79	432.58
	438.35	440.48				
Fe II	300.26	306.22	307.72	313.54	315.42	316.78
	317.75	318.31	318.67	319.29	319.38	319.6
	321.04	321.34	325.9			
Cr I	300.5	301.37	301.48	301.76	301.84	302.06
	302.43	303.02	303.42	303.98	304.08	305.38
	323.77	343.36	357.43	358.43	359.34	360.53
	363.66	363.98	384.94	385.89	396.36	397.66
	398.38	399.11	425.43	427.48	428.97	520.45
	520.6	520.84				
Cr II	302.66	305.01	312.26	312.5	312.86	313.2
	313.66	314.72	315.22	318.06	320.92	321.74
	333.98	334.26	334.78	336.02	337.83	337.94
	337.98	338.26	339.14	339.3	340.24	
Mn I	323.68	324.85	353.19	354.78	382.35	403.08
	403.3	403.44	403.57	404.14	404.87	445.16
	476.23	478.34	482.35			
Mn II	346.03	347.4				
Ni I	300.36	301.19	303.79	305.08	305.76	310.15
	323.29	336.96	338.06	341.48	344.62	345.84
	346.16	347.25	349.3	351.03	351.5	352.45
	356.64	361.94				
Ni II	308.7	347.14	351.39			

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