

Elemental Detection by LIBS Technique

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1 Certificate

This is to certify that the work contained in this project report titled “Elemental detection by LIBS Technique” has been carried out by Mr. Satyanarayan Ray Pitambar Mohapatra, Roll No. Y2590 under my supervision for the courses PHY563 and PHY565.

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(Project Supervisor)
November 14, 2003

Abstract

LIBS technique was used to detect trace of elements like sodium(Na) and magnesium(Mg) in water. A detection limit of 8 ppm for the detection of sodium was achieved. Using the calibration of the instrument, concentration of a sodium in a solution was ascertained. Impurity concentration of sodium in $MgSO_4$ solution was estimated.

2 Introduction

LIBS(Laser Induced Breakdown Spectroscopy) is seen as a capable tool of detection in the field of elemental analysis. When a pulsed laser with an optimum energy is irradiated on the surface of a sample, a small amount of the sample is vaporised and subsequently removed from the surface. The ejected material cloud known as plume shows several emission line characteristics of the atoms or molecular species in it.

2.1 Advantages of LIBS Technique

- LIBS method can be used for rapid and remote analysis.
- Real time analysis is possible.
- Complete elemental coverage can be achieved.
- The analysis sample size is very small.
- A very small detection limit can be achieved. (ppm/ppb)

2.2 Possible applications of LIBS

- Detection of elements in nuclear reactors.
- Detection of elements in deep sea.
- Detection of elements in other planet[1].
- Environmental monitoring like determination of soil contamination and particulates.
- Material analysis, e.g. for metals, plastic etc.
- Forensics and biomedical studies, e.g. teeth and bones analysis.
- Military and Security applications, e.g. to look for traces of biological warfare materials like Anthrax.
- Art restoration/conservation.

2.3 Advantages of water based samples

- Relatively low concentration of solution can be prepared.
- Solutions in water are more homogeneous than solid.
- For the homogeneity nature spatial variation of concentration is not there.

2.4 Why Na ?

- Easily available element to start with.
- A possible application regarding Na is to determine Na concentration in sea ice[2].
- This method may find its application in determination of Na concentration in blood and cells.

3 Experimental Set up

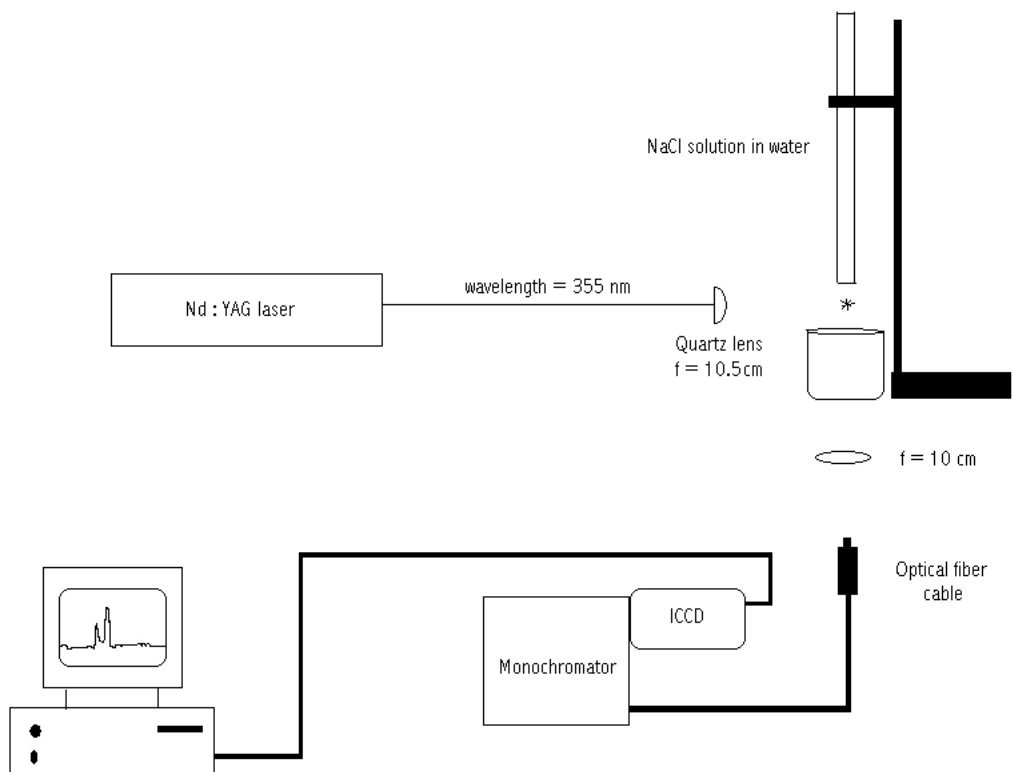


Figure 1: Set Up

3.1 setup specifications

Wavelength of laser radiation	355 nm
Energy of laser radiation	18 mJ
Focal length of plano-convex quartz lens	10.5 cm
Focal length of imaging lens	10 cm
Pulse repetition rate	10 Hz
Gate width for time-integrated spectra	2 μs
Gate width for time-resolved spectra	500 ns
Gate delay with respect to laser pulse	300 ns

4 Experiment

First a known amount of $NaCl$ was taken in a known volume of distilled water. That particular concentration of $NaCl$ solution was taken in the burette. It was taken care of that the flow rate through the burette was continuous and steady¹. Laser radiation from the Nd-Yag Laser was focussed on the water stream by using a quartz lens² to produce plasma. The image of the plasma was focussed into the optical fiber cable slit. With the help of the monochromator and subsequently the ICCD(Intensified Charge Coupled Device) the spectrum was captured and stored in the computer. Both time integrated³ and time resolved⁴ spectra were recorded. The intended lines were identified using standard table of wavelength. Then the concentration of the $NaCl$ solution was changed to half. This was achieved by discarding half of the solution and then diluting the solution by distilled water. The spectrum was captured for the new concentration of solution. This process of changing the concentration and recording the intensity of Na I 589 nm ($3s2S - 3p2P^0$)($\Delta J = 1$)(D1) and Na I 589.6 nm ($3s2S - 3p2P^0$)($\Delta J = 0$) (D2) lines were repeated upto the point where either of the lines were difficult to observe above the background. Using the observation a detection limit was established by the $3\sigma/m$ formula, where σ is the standard deviation and m is the slope of the linear fit at low concentration. To achieve a lower detection limit the experiment was repeated with initially taking a lower concentration. This time the concentration of Na in the solution was changed by small amount.

Single element analysis is useful only if its concentration can be determined in a solution where other elements are present. For this reason a solution of magnesium ($MgSO_4$) in water was tested with sodium. In this part a known amount of $MgSO_4$ was taken in a known volume of water. The $MgSO_4$ spectra was observed for the whole range of ICCD detection range to look for any overlap with Na lines. At 589 nm and at 589.6 nm i.e. the Na D1 and D2 lines were present. It was inferred that impurity of Na was present in $MgSO_4$. Then a known amount of $NaCl$ was added to the $MgSO_4$ solution. From the intensity using the previous calibration curve the concentration of Na was determined.

¹Unsteady flow would result in defocussing of both incident laser radiation and plasma image.

²UV radiation is absorbed by ordinary glass lens.

³Time integration gives a temporal average for the intensity.

⁴Time resolved data gives information about how the plasma intensity dies down with time.

5 Observation and analysis

5.1 Typical sodium lines

A typical Na I 589 nm ($3s2S-3p2P^0$)($\Delta J = 1$)(D1) and Na I 589.6 nm ($3s2S-3p2P^0$)($\Delta J = 0$)(D2) lines are given below in Fig. 2.

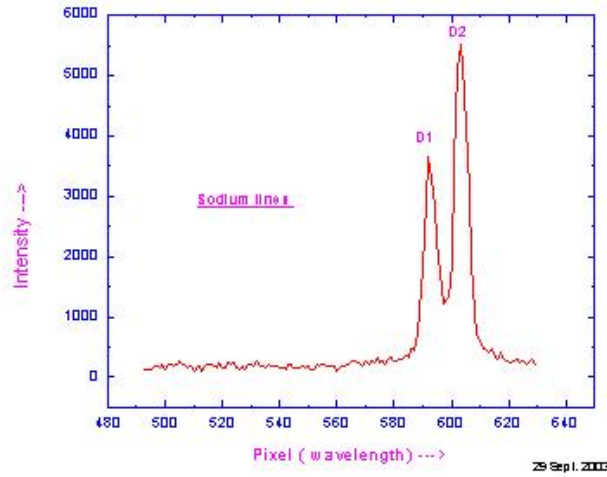


Figure 2: Sodium D1 589 nm and D2 589.6 nm lines

5.2 Determination of gating time

Optimum gating time was obtained by trial and error method to have *optimum detection limit*. The *optimum detection limit* depends upon both the *spatial* and *temporal* variation of plasma expansion in air[3,4]. The *spatial* trend can be studied by positioning the slit of the optical fiber cable at different positions.

The background hinders having a low detection limit. Fig. 3 is the time resolved graph of a typical background obtained in my experiment.

There can be two main sources of background radiation. One due to the *detector noise* and the other due to the *plasma continuum*. The detector noise can be corrected by taking background corrected signal. The *plasma continuum* is obtained due to the phenomenon of *bremstrahlung*. Had the background be only due to the *detector noise*, it could have been reduced by using some averaging process, like background correction. But the *bremstrahlung*

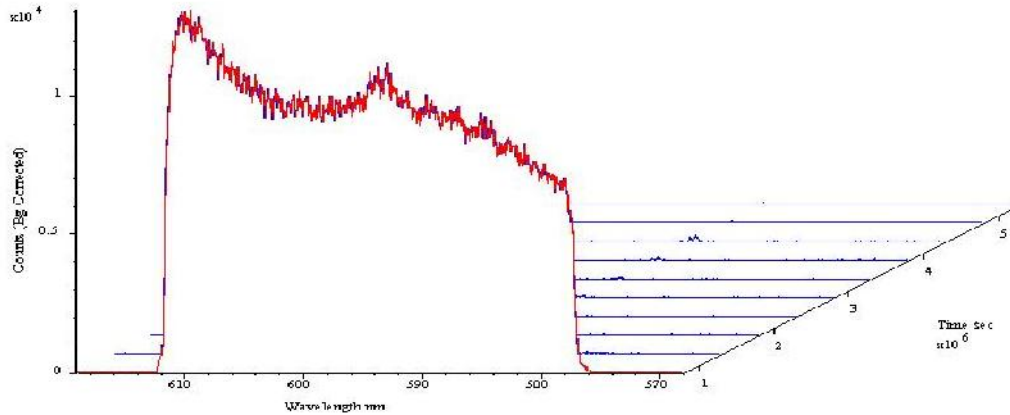


Figure 3: Background due to *plasma continuum* and *detector noise*

background cannot be reduced by statistical averaging process. It decays with time. So by choosing an appropriate gating time and thereby ensuring to observe the spectra after the *plasma continuum* dies out we can get good signal to background ratio. So first, the signal intensity was monitored as a function of gate width of the laser pulse for a fixed delay time to determine the maximum signal intensity. Then keeping the gate width fixed, the delay time was varied until the continuum emission (*bremssstrahlung*) decayed and discrete line features were revealed. The time resolved graphs of D1 and D2 lines for an optimum gating time of slits is given in Fig. 4 and Fig. 5. The improvement, i.e. reduction of background, in the Fig. 4 and Fig. 5 compared to Fig. 3 can be noted.

5.3 Calibration Curve for NaCl

The calibration curve for the D1 line of *NaCl* in the first run of the experiment is shown in Fig. 6. The experiment was started with 1622 ppm concentration of Na. A *detection limit* of 116 ppm was obtained here. The popular notion of *detection limit* is the minimum amount of substance an instrument can detect. This definition is not an objective definition. The main subjectivity of the definition is due to fact that in one experiment there is no fixed concentration below which the signal may not be observed. Also it may so happen(it also happened in my experiment) that after some concentration the signal would be observed perfectly but no information about the concentration can be obtained from the intensity. An objective definition of *detection limit* would be “the concentration resulting in a signal corresponding to 97.7 % of confidence level” [4]. This is given by the $3\sigma/m$ formula. Where σ is the standard deviation of the linear fit and m is slope of the linear fit at low concentration. The linear nature of the fit is evident from the graph (Fig. 6).

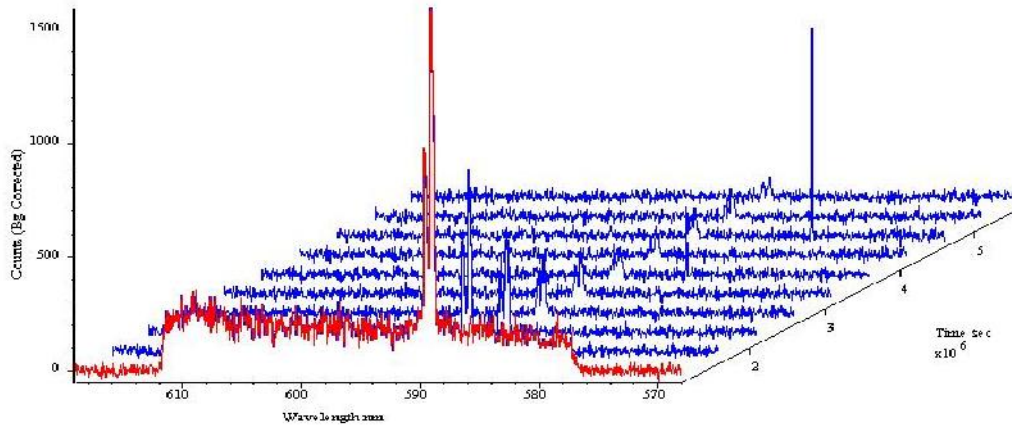


Figure 4: Gate delay 300ns

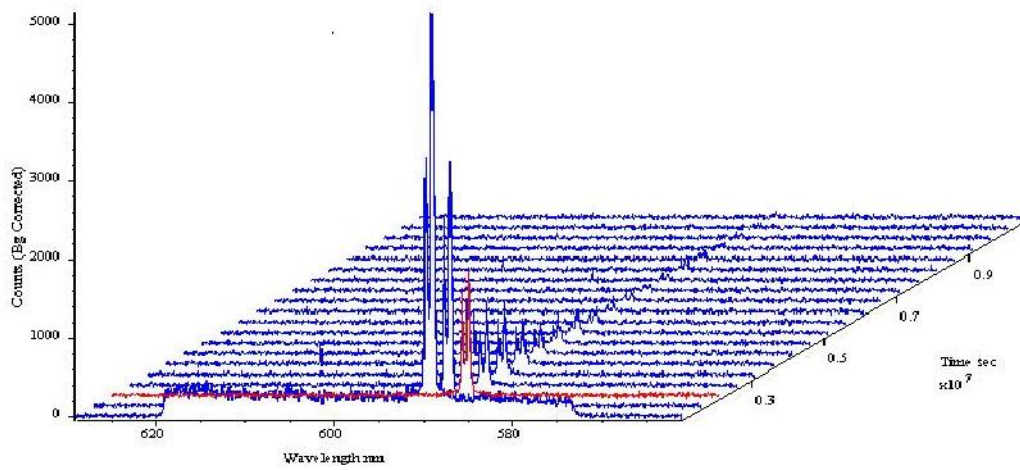


Figure 5: Gate delay 300ns

Fig. 7 is the calibration curve for D2 line of *NaCl* obtained in the first run of the

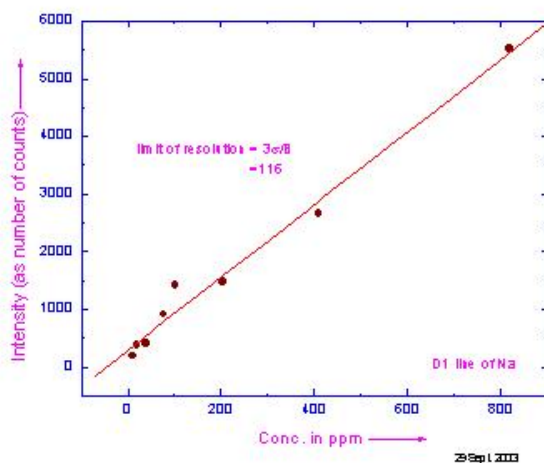


Figure 6: D1 calibration with *detection limit* 116 ppm

experiment. A detection limit of 123 ppm was obtained here.

The experiment for $NaCl$ solution was repeated once more. This time the observation was started from a lower value of concentration (59 ppm). Now more care was taken while taking observation. After each observation the burette was rinsed with distilled water. Fig. 8 is the calibration curve for D1 line of Sodium. Here a detection limit of 7.8 ppm was achieved.

Fig. 9 is the calibration curve for D2 line of Sodium. Here a detection limit of 19 ppm was achieved.

5.4 Na impurity calculation in $MgSO_4$

First a known quantity of $MgSO_4$ was taken in 400 ml of distilled water. All the transitions within the ICCD detection range were observed. It was observed that Na D1 and D2 transitions were present there. Using the previous calibration done, the concentration of Na impurity was estimated to be 351 ppm. Then to the $MgSO_4$ solution a known amount (106 ppm) of $NaCl$ was added. So now the concentration of Na would have been $351 + 106 = 457$ ppm. From the observed line intensity the new concentration was estimated to be 516 ppm with a deviation of 11% from expected value. Nothing much can be inferred from it. More such type of observations are required to test the technique's predictive power.

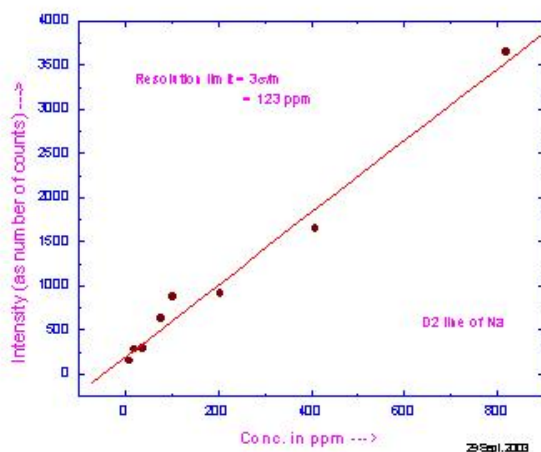


Figure 7: D2 calibration with *detection limit* 123 ppm

6 Summary and Conclusion

In this semester the main thrust in my project was to determine the detection limit of some elements and to determine concentration of a particular element in a mixture where other elements are also present. I started with sodium. A detection limit of 8 ppm was obtained for sodium in water. The concentration of sodium in magnesium solution was estimated. A deviation of 11% was observed.

But in an actual setup to determine concentration, the following problems are to be fixed and some improvements are to be made. They are,

- It is desirable for an LIBS based elemental detection apparatus to use a single or atmost 2/3 wavelengths. Suitable wavelength for a particular element is to be determined. So in the presence of a number of elements an appropriate wavelength for laser radiation is to be determined. An appropriate wavelength means, a wavelength by which a wide range of elements can be distinguished.
- To obtain an *optimum detection limit*, both temporal and spatial expansion of plasma in air should be studied. The study should be based on some plasma models and the results should be interpreted by the models.
- This semester all the experiments were performed using 18 mJ of laser energy. But a suitable energy value should be chosen.

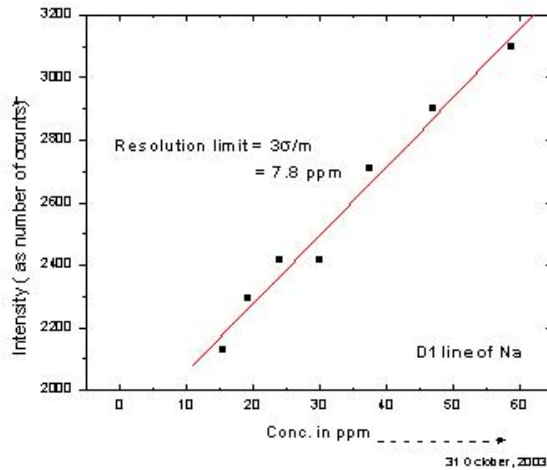


Figure 8: D1 calibration with *detection limit* 7.8 ppm

- This semester only magnesium and sodium were observed. Both of these elements do not have much lines within detector range. Elements like Cr, Ni, Fe and Cd should be tried. Multiple lines of these elements would help in determination of plasma parameters like *plasma density* and *plasma temperature*.
- When a number of elements are present, then there may be some overlap of the lines. So to distinguish the lines of different elements some pattern recognition algorithms, e.g. the Mahalanobis distance algorithm, should be implemented[5].
- The LIBS method should be compared with other standard and authentic method like *induction coupled plasma*.
- Salt solution of sodium and magnesium can be taken in the form of ice cubes. As the laser probes a very small area, their LIBS analysis can be made with out destroying the ice cubes. This can be used to calibrate the instrument for analysis of concentration of elements in polar ice (e.g. Antarctica)[2].

Some of the above problems and suggested improvements would be the topic of my interest next semester.

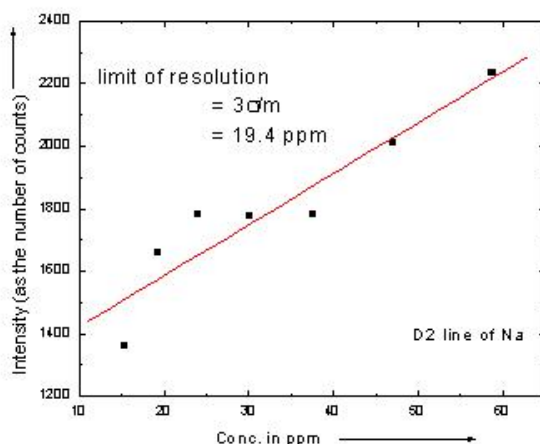


Figure 9: D2 line with *detection limit* 19 ppm

7 Acknowledgments

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8 References

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