Temperature and Electron Density Determination on Laser-Induced Breakdown Spectroscopy (LIBS) Plasmas: A Physical Chemistry Experiment

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Laboratory Experiment

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Temperature and Electron Density Determination on Laser-Induced Breakdown Spectroscopy (LIBS) Plasmas: A Physical Chemistry Experiment

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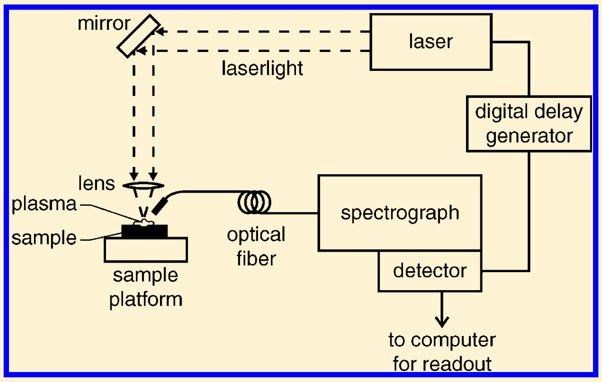
Ⓢ *Supporting Information*

ABSTRACT: This laboratory is designed for physical chemistry students to gain experience using laser-induced breakdown spectroscopy (LIBS) in understanding plasma diagnostics. LIBS uses a high-powered laser that is focused on the sample causing a plasma to form. The emission of this plasma is then spectrally resolved and detected. Temperature and electron number density of the plasma can be determined from the characteristics of the spectrum. Temperature was calculated using the Boltzmann plot method, whereas electron density was determined from Stark broadening considerations. Students learned how to use the information provided by the LIBS spectrum to obtain plasma temperatures and electron densities for various samples. This experiment is appropriate for a physical chemistry course.



KEYWORDS: *Upper-Division Undergraduate, Laboratory Instruction, Physical chemistry, Hands-On Learning/Manipulatives, Atomic Spectroscopy, Lasers*

Laser-induced breakdown spectroscopy (LIBS) is a growing technique in atomic spectroscopy due to its many advantages. This simple method involves little or no sample preparation, does not require extensive operator training, and delivers spectra with high sensitivity capable of real-time analysis. LIBS utilizes a high-powered laser, coupled with a mirror and lens, to focus a laser pulse onto a sample. Sample types can be wide ranging because optical absorption processes initiate LIBS sampling, thus, allowing analysis of solids, liquids, and gases.[1] Once the energy from the laser pulse heats, ablates, atomizes, and ionizes the sample material, a plasma is formed. The light of the plasma is then spectrally resolved and detected by a spectrograph and a detector. Both quantitative and qualitative information, such as elemental composition, can be deduced from the resulting plasma spectrum. Emission line properties such as widths, shapes, and shifts can provide information on plasma temperature and electron density.[2]

Plasma temperature is an important thermodynamic property due to its ability to describe and predict other plasma characteristics such as the relative populations of energy levels and the speed distribution of particles. The method used in this laboratory experiment is the Boltzmann plot method, which assumes that local thermodynamic equilibrium (LTE) is met within the plasma. Under normal air pressure, it has been shown through approximations that LTE is usually met after a couple hundred nanoseconds after plasma formation using LIBS with irradiances greater than 10^8 W/cm^2. The Boltzmann plot method is a common way of reporting plasma temperatures in the LIBS community and is more precise than alternative methods, such as the two-line method of the Boltzmann distribution. The two-line Boltzmann method compares the ratios of relative intensities of two lines that have known degeneracies, transition probabilities, and upper-energy values. The Boltzmann plot method uses multiple lines that have known degeneracies, transition probabilities, and upper-energy values to graphically determine the temperature. The temperature that is calculated from this method represents an average temperature of the plasma.[2]

Electron density describes the number of free electrons per unit volume. There are several credible techniques used to determine electron density, including plasma spectroscopy, microwave and laser interferometry, and Thomson scattering.[3] The determination of electron density by linear Stark broadening of spectral lines, as used in this lab, is a well-established technique.[3] Line broadening in LIBS plasmas is caused primarily by Doppler width and the Stark effect. Doppler width is dependent only on the temperature and atomic mass of the emitting species; this type of broadening is disregarded in this experiment as the Doppler width of the hydrogen line used is usually between 0.04 and 0.07 nm.[2] The Stark effect is considered a type of pressure broadening that involves interactions of radiators and neighboring particles. In plasmas, these interactions are caused by collisions of ions and to a lesser extent electrons. The Stark effect is mainly responsible for the line broadening of the hydrogen line used in this experiment. The full-width at half maximum (FWHM) of the atomic line (in our case, the hydrogen line at 656.5 nm) can be measured easily and is used to determine the electron density of the LIBS plasma.[2−4]

This experiment is designed for a physical chemistry laboratory and shows students how spectral information can be used to calculate plasma temperatures and electron densities. The student lab handout is included in the Supporting Information. Recently, a lab experiment was published in this *Journal* showing how LIBS can be incorporated into an instrumental analysis course.[5] The learning objectives for this experiment are (i) to use and understand the theory associated with LIBS, (ii) to visually see the differences between the LIBS spectra of different substances, (iii) to learn how to use the online NIST database to obtain spectral information on specific atomic lines, and (iv) to learn how to calculate plasma temperatures and electron density from emission lines in a LIBS spectrum.

■ MATERIALS AND METHODS

Materials

There is no sample preparation for this laboratory experiment. The samples used were metal electrodes consisting of aluminum (Al), brass, bronze, carbon (C), copper (Cu), iron (Fe), magnesium (Mg), Nickel (Ni), lead (Pb), stainless steel, and titanium (Ti) (metal electrodes, product code: METELECT12, Miniscience Inc., Clifton, NJ).

Equipment

The experimental setup remained constant throughout this lab experiment. A Nd:YAG laser (1064 nm) (Surelite II, Continuum, Santa Clara, CA) was operated at 10 Hz and 75 mJ per pulse, and a 50 mm focal length lens was used to focus the laser pulse onto the sample. The spot size on the sample was approximately 0.080 cm; this produced an approximate power density of 2.5 GW/cm^2. An optical fiber (QP1000-2-UV-VIS, Ocean Optics, Dunedin, FL) placed near the sample captured the light emitted from the plasma. The light was then spectrally dispersed and detected with an echelle spectrograph and ICCD (echelle, SE200, Catalina, Tucson, AZ; and ICCD, DH-734-18F-03, IStar, Andor Technology, Belfast, Ireland); the approximate resolving power of the echelle and ICCD is 1700. All data were taken at atmospheric pressure using 1 μs time delay and a 20 μs gate width; the detector waited 1 μs to view each pulse and then analyzed each pulse for 20 μs. Thirty pulses were averaged per trial; because the laser was operated at 10 Hz, this resulted in a 3 s experiment per data point. The signal was integrated on the detector chip. A digital delay generator (BNC model 575-4C digital delay and pulse generator, Berkeley Nucleonic Corp., San Rafael, CA) effectively controlled the timing between the laser and the ICCD. A typical LIBS setup has been shown previously.[4] A list of possible lasers, spectrographs, and detectors is included in the Supporting Information.

Experimental Procedure and Data Workup

The students were given two samples from the metal electrode set to analyze. Each sample was analyzed five times and the data were processed using Microsoft Office Excel 2010. Plasma temperature was determined using the Boltzmann plot method. The spectral line radiant intensity is given by

$$I = h\nu AN/4\pi = (hcN_0 gA/4\pi\lambda Z)\exp(-E_u/kT) \quad (1)$$

where I is the intensity of the transition, h is Planck's constant, ν is the line frequency, g is the degeneracy, A is the transition probability, N is the absolute number or number density, c is the speed of light, N_0 is the total species population, λ is the wavelength, Z is the partition function, E_u is the energy of the upper state for emission, k is Boltzmann constant, and T is the temperature.[2] To effectively perform a graphical analysis of the spectral data, eq 1 is rearranged to

$$\ln(I\lambda/gA) = -E_u/kT - \ln(4\pi Z/hcN_0) \quad (2)$$

For each sample, $\ln(I\lambda/gA)$ was plotted against E_u (in eV) to illustrate the Boltzmann plot. About five spectral lines were used for each trial. A straight-line approximation of the plot was fit to the data to illustrate the Boltzmann distribution.[2] Because the slope of the line is equal to $-1/kT$, the temperature can be easily calculated. Temperatures are reported in Kelvin. A typical Boltzmann plot is shown in Figure 1. The students were required to make five individual Boltzmann plots for each trial and calculate a temperature for each plot; they then calculated an average temperature.

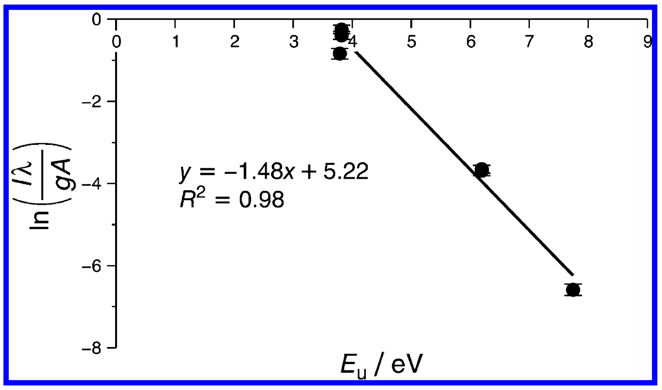


Figure 1. A typical Boltzmann plot for the brass electrode. Each point represents an average of the five trials at a given wavelength.

The electron density of the plasma was calculated using the Stark broadened line width of the hydrogen line at 656.5 nm; this hydrogen line corresponds to the Balmer alpha line. Once the maximum intensity of the hydrogen line was found, the full-width at half-maximum intensity is recorded. The electron density in the plasma is calculated using the following equation for the linear Stark line width for hydrogen lines:

$$N_e = 8.02 \times 10^{12}[\Delta\lambda_{1/2}/\alpha_{1/2}]^{3/2} \quad (3)$$

where N_e is the electron density, $\Delta\lambda_{1/2}$ is the measured FWHM of the hydrogen line, and $\alpha_{1/2}$ is the reduced wavelength. The reduced wavelength is a function of the temperature and electron density and the values are provided in Griem's 1974 Appendix IIIa.[4,6] A program was written that calculates a reduced wavelength for each N_e supplied in Griem's appendix at a specific temperature. Then by interpolation of these results, the program determines the relationship between N_e and the calculated reduced wavelengths. Using this relationship and eq 3, the N_e (and $\alpha_{1/2}$) can easily be calculated at any temperature.[4,6] The developed program was set up to calculate the electron densities at 10,000; 15,000; and 20,000 K. The students used the temperature that was closest to their calculated Boltzmann temperatures; they only had to enter their FWHM value on the spreadsheet and the program

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calculated the N_e. This program is discussed more thoroughly in the Supporting Information.

HAZARDS

The Nd:YAG laser is a class IV laser product that produces both visible and invisible laser radiation. It is necessary to avoid eye and skin exposure to the radiation. Laser safety goggles should be used at all times when the laser is in use; goggles appropriate for the wavelength of radiation should be used. Also, proper signage and door interlocks should be in place to protect students and faculty when entering the room. The ablation of the sample produces minimal vapor. There is typically no inhalation hazards associated with experiment because the samples being ablated are not in the near proximity of the students; the students are standing about 2 to 3 feet away from the samples.

RESULTS AND DISCUSSION

This lab was completed over a two-week period. During the first week, the students took the LIBS data on their samples. Acquiring the LIBS data is very quick; each group takes less than 10 min to take and save the actual data. Therefore, during that first week, another theoretical lab was supplied for the students to perform while the other students were gathering their actual LIBS data. During the second week, the students were given the 3-h lab period for their data analysis, which involved plasma temperature and electron density determinations.

For the plasma temperature determination, the students were supplied information on the wavelengths they needed to use for each sample type (this information is supplied in the Supporting Information). The specific emission lines were chosen to produce a range in upper energies of about 2 eV; this was done to provide a larger range for the x axis values (upper energies) on the Boltzmann plots. These emission lines were determined experimentally for each sample type; sometimes, the same emission lines could be used for a different material that contained a given element. There are many books and databases of atomic lines that lists line types, degeneracies, upper energies, and transition probabilities.[7−9] All of this information is included in the Supporting Information. The students were shown how to use the on-line NIST database[7] and were required to look up the degeneracies, upper energies, and transition probabilities for their specific emission lines. The students plotted the spectrum of their material to determine the intensity values of their specific emission lines. For simplicity purposes, the intensity values were read as the highest point on the emission peak of interest directly from Microsoft Excel. Upon acquiring the needed information (line emission intensities, upper energies, transition probabilities, and degeneracies), the students were able to create their Boltzmann plot and calculate their plasma temperature. The students analyzed each sample five times; they created five Boltzmann plots per sample and were required to report the average temperatures with their percent relative standard deviations.

For the electron density determination, the students plotted the emission spectrum in the region of 656.5 nm to determine the fwhm of the hydrogen line. As the resolving power of the echelle used in this experiment is approximately 1700, lines should be resolved if they are separated by 0.38 at 656.5 nm. The FWHM of this hydrogen line is approximately 1 nm; this broadened line is due to Stark broadening. The Doppler effect is neglected since the Doppler width is below our resolution (the Doppler width ranges from 0.04 to 0.07 nm for a temperature range of 7,000−20,000 K).

The laser pulse not only excites the sample but also excites the ambient air. The hydrogen emission line produced comes from excitation of the air. The students determined the FWHM of the hydrogen line and used the supplied Microsoft Excel program to calculate the electron density at a specific temperature. The observed FWHM of the hydrogen lines for the various electrodes analyzed ranged from 0.96 to 1.3 nm. Figure 2 shows a spectrum of a typical hydrogen line. As can be seen, the observed FWHM is approximately 1 nm. The students reported the average electron density with their percent relative standard deviation. These results are shown in Table 1.

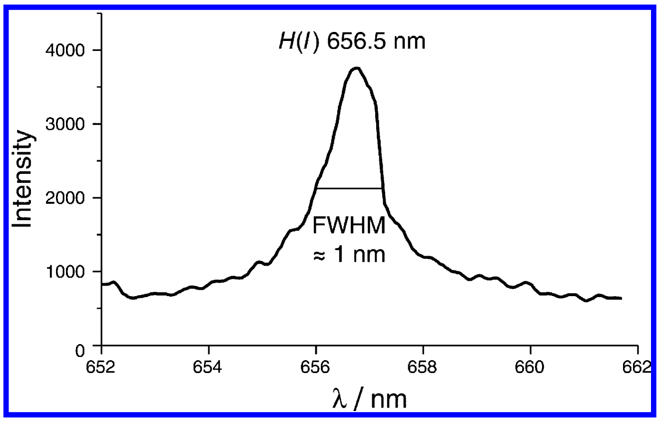

Figure 2. The observed hydrogen line for one trial on the brass electrode; note that the hydrogen emission comes from air excitation. This broadened line is due to Stark broadening.

This experiment reveals basic temperature and electron density parameters for many substances, thus, illustrating the wide-range of LIBS applications. The majority of the samples produced highly reproducible results with percent relative standard deviations well under 10%. The electron density calculations have a slightly wider range of %RSDs; this is probably due to a combination of matrix effects that can occur with LIBS analyses and variations in excitation of air. Generally, the students enjoyed using the LIBS instrumentation and being able to visually see the differences in the LIBS spectra from the various samples. Initially, some of the students found some difficulty in the data analysis. However, having a whole lab period to discuss the theory and calculations with the students gave them the proper background to perform the calculations correctly through their increased knowledge level and the data analysis became much easier and quicker. It is also important to note that some groups were able to finish the full data workup during the 3-h lab period.

SUMMARY

The students gained a valuable experience using LIBS. They learned how to use the NIST database for obtaining the spectral information needed for the Boltzmann plots, how to make and prepare Boltzmann plots to calculate plasma temperatures from spectral data, and how to measure the FWHM of the hydrogen line to calculate the electron density of the plasma. These results are pertinent for a physical chemistry course. Furthermore, this lab experiment introduces another

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Table 1. Average Plasma Temperature and Electron Density for the Electrodes Tested

Electrode Type	Average Temperature/K	%RSD[a]	Element Used for Temp. Analysis[b]	Average Electron Density/($\times 10^{17}$ cm^{-3})	%RSD[a]
Aluminum	7730	2.02	Al (I)	1.03	4.60
Brass	7830	1.48	Cu (I)	1.04	5.29
Bronze	7790	0.60	Cu (I)	1.02	7.33
Carbon	13200	2.54	Ca (II)	1.09	13.45
Copper	7720	0.98	Cu (I)	1.00	1.90
Iron	10600	4.83	Fe (I)	1.03	8.53
Lead	16600	1.39	Pb (I)	1.00	5.11
Magnesium	8550	5.86	Mg (I)	1.09	5.79
Nickel	20200	1.70	Ni (I)	1.11	4.66
Stainless Steel	9670	2.66	Fe (I)	1.02	1.00
Titanium	13600	3.10	Ti (II)	1.16	4.01

[a]%RSD stands for percent relative standard deviation. These results are averaged based on five spectra per sample analyzed. Five Boltzmann plots were made for each spectrum and the average temperature is reported; five measurements of electron density were also performed and the average electron density is reported. [b]The lines labeled as (I) represent neutral atomic lines and the lines labeled as (II) represent singly ionized lines. Please note in the carbon electrode, calcium is a minor contaminant in this sample.

way to incorporate LIBS into the undergraduate laboratory. All of the learning objectives were met in this laboratory experiment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Directions for the instructor; directions for the student; directions to change the temperature program; electron density Excel spreadsheet. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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