



Theoretical and experimental investigation of matrix effects observed in emission spectra of binary mixtures of sodium and copper and magnesium and copper pressed powders☆



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ABSTRACT

The goal of this work was to investigate the matrix effect of copper in the presence of sodium or magnesium in a laser-induced plasma. Varying amounts of copper were mixed and pressed with a constant amount of sodium or magnesium and a stearic acid binder. Experimental parameters such as delay time and laser pulse energy were varied to observe trends in the emission intensity of the Na I 588.99 nm, Na I 589.59 nm, Mg I 277.98 nm, and Mg II 279.08 nm lines. Experimental observations are supported by theoretical calculations and modeling that show the Na I and Mg I emission intensities increase in the presence of copper while the Mg II line intensity decreases due to the increase in electron density (N_e) of the plasma when copper is added. The increase in electron density changes the population of the atomic species within the plasma through an increase in recombination of ions with electrons, shifting the populations toward more neutral states, providing an explanation for the observed matrix effects found in these, and many previous, studies.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is an atomic emission technique capable of multi-element analysis [1,2]. The experimental setup is relatively simple and highly configurable for a variety of applications [3–9]. LIBS requires little to no sample preparation and is minimally destructive, removing nanograms to micrograms per analysis. Due to these reasons, many are interested in using LIBS for rapid qualitative and quantitative analysis. LIBS has been used successfully to qualitatively determine a sample's composition but more interest in accurate quantification has emerged. Typically calibration standards are required for accurate quantification; however, there remains concerns in terms of accuracy. One of the major areas of inaccuracies are matrix effects.

Matrix effects are known and discussed in the LIBS literature extensively [10–20]. Several different types of matrix effects exist: physical and chemical, and both of these may affect the measured emission from a sample. Physical matrix effects can be described in terms of the particular form of the target (oxide, metal, etc) or the sample

composition (metal, soil, plant, etc) [13]. They play a role in LIBS signal intensity and ablation efficiency by affecting the laser-sample coupling and are more in line with the traditional solution phase definitions of matrix (solution composition). Chemical matrix effects are best defined in the community by Clegg [14] “as chemical properties of the material that influence the ratio of a given emission line to the abundance of the element producing that line.” Hahn [10] also describes matrix effects as “the role of concomitant mass on the physics of complete particle vaporization and ultimately on the analyte response within the plasma.” In this paper, we aim to explore the underlying physics behind chemical matrix effects in terms of the atomic species role within the laser-induced plasma.

Many groups have attempted to minimize or eliminate matrix effects through post processing of data or sample manipulation. Ciucci [15] describes a calibration free method to eliminate matrix effects. The method assumes that the plasma is in local thermal equilibrium (LTE) and optically thin. The temperature can then be extracted from the spectrum and in combination with integrated emission intensity for each element, the instrument response curve, and the atomic parameters of the transition, a concentration is determined for each element. The authors claim this data treatment procedure eliminates matrix effects and does not require traditional calibration standards. Gornushkin [16] also used a calibration-free method to correct for matrix effects by normalizing the spectral emission by the surface density

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Table 1

Sample description including mass (grams), moles, and Na/Cu or Mg/Cu ratio are shown.

Samples	g Na ₂ CO ₃	g Mg(OH) ₂	g CuO	g Stearic acid	Moles Na	Moles Mg	Moles Cu	Ratio Na/Cu	Ratio Mg/Cu
Na only	0.1			2.9	1.89E-03		0		
1: 1 Na:Cu	0.1		0.15	2.75	1.89E-03		1.89E-03	1	
1: 3 Na:Cu	0.1		0.45	2.45	1.89E-03		5.66E-03	3	
1: 9 Na:Cu	0.1		1.35	1.55	1.89E-03		1.70E-02	9	
Mg only		0.1		2.9		1.71E-03	0		
1:3 Mg:Cu		0.1	0.41	2.49		1.71E-03	5.15E-03		3
1:9 Mg:Cu		0.1	1.22	1.68		1.71E-03	1.53E-02		9

of the sample. Other authors have attempted to compensate for matrix effects through normalization of the data to the total integrated emission intensity [17] or to electron plasma temperatures [18–20].

A specific motivation for this work was the study of Diwakar et al. [21], who studied the changes in Na or Mg line emission resulting from addition of other species to the sample, so-called localized matrix effects. Their measurements considered aerosolized targets in which the concentration of the analyte solution could be systematically varied. The authors reported a $1.53 \times$ signal enhancement of sodium in the presence of copper for a binary aerosol mixture of 1:9 Na:Cu. The authors also investigated a magnesium and cadmium aerosol mixture and found that the Mg II signal decreases as a function of delay and at a fixed delay time, the increase of Cd I and Cd II is observed as the mass fraction increases (1:5, 1:11, and 1:17 Mg:Cu). The author's main conclusions were that the analyte emission (Na, Mg) from aerosol particles increases in the presence of other elements and that at longer delay times, these effects are minimized. Therefore, to reduce matrix effects observed in aerosolized particles, one should acquire LIBS spectra at longer delays [21]. The enhancement of emission lines is illustrated very well in this study with some description of plasma dynamics. However, how the emission intensity relates to electron density was not thoroughly discussed. Preliminary calculations by us were able to confirm the findings of [21], specifically that addition of Cu to a pure sodium-based plasma resulted in a significant increase of the line intensity of the Na I 589 nm lines. This enhancement of the line intensity results from the increased electron density of the plasma formed when Cu is present; the increased electron density promotes recombination and increases the population of the neutral Na atoms in the plasma, resulting in enhanced line intensity. To further explore such effects, we initiated a series of experiments in which we explored similar binary mixtures and investigated these matrix effects. Mg is also of much interest in this regard, since the presence of prominent lines from Mg I and Mg II in similar wavelength ranges allows exploration of whether the intensity of emission lines can also be *decreased* due to matrix effects. Here, we follow and extend the work of Diwakar et al. [21] and measure the enhancement of sodium and magnesium in the presence of copper in pressed powders.

2. Experimental

2.1. Sample preparation

Pressed pellets were prepared in varying mole ratios of sodium and copper and magnesium and copper with a stearic acid binder, Table 1. The chemicals used were sodium carbonate (Na₂CO₃, Sigma–Aldrich), copper oxide (CuO, Sigma–Aldrich), magnesium hydroxide (Mg(OH)₂, Sigma–Aldrich), and stearic acid (C₁₇H₃₅CO₂H, Sigma–Aldrich). The amount of sodium or magnesium remained constant while the amount of copper added was systematically increased. The total mass of each pressed pellet was 3 g. The samples were prepared with the following mole-to-mole ratios of Na:Cu and Mg:Cu: 1:1, 1:3, and 1:9. Na only and Mg only were prepared in stearic acid with the same concentration of respective series to serve as a reference point. Each mixture was combined with a mortar and pestle for 5 min then pressed into 1 in. discs for 10 min at 34,000 lbs.

2.2. Instrumentation

The LIBS experiments were carried out by using a Nd:YAG laser (CFR 400 Quantel USA) with a maximum output energy of 400 mJ per pulse at 1064 nm operating at a repetition rate of 20 Hz (shots per second) and a pulse width of 8 ns. The delay time was varied between 0.5 and 5 μ s with a constant gate width of 1 μ s. An excitation energy of 34 mJ at 5 Hz was used for Na:Cu delay study experiments while an energy of 54 mJ at 5 Hz was used for the Mg:Cu experiments. The focal spot diameter is approximately 350 μ m and the laser pulse duration is 8 ns, which implies a laser irradiance of approximately 6×10^9 W/cm². As shown in Fig. 1, the laser was reflected off a 45-degree mirror and then through a focusing lens to generate a plasma on the sample. The plasma emission was collected approximately 20° from the laser path by collection optics which included two lenses coupled to a fiber optic cable approximately 2 in. from the plasma. The fiber transmitted the plasma emission to the high-resolution spectrograph, which has a maximum resolving power of 75,000 (Double Echelle Monochromator, DEMON, LTB Instruments Berlin, Germany). However, in practice, the resolving power in the measurements shown here was approximately 38,000. Every spectrum shown is an average of 50 laser pulses.

2.3. Theoretical modeling

Our theoretical modeling of the emission from LIBS plasma follows closely recent work by Colgan and Johns [22–24] using the ATOMIC code. We use the Los Alamos suite of codes (for an overview, see [25]), and begin with atomic structure calculations [26,27], which result in a set of energy levels, transition probabilities, and photoabsorption cross-sections. The energy levels are adjusted to their experimentally derived NIST values [28] in an automated manner as discussed in detail in [22]. The GIPPER code [29] is used to compute photoionization cross-sections used to compute the free-bound contribution to the emissivity. Our modeling aims to include a sufficient number of energy levels such that the partition function is well converged, while keeping our calculations computationally tractable. For Na, we included 311 levels for Na I and 786 levels for Na II. For Mg I, we included 526 levels, and for Mg II, we retained 239 levels. For Cu, we included 880 energy levels for Cu I and 3731 levels for Cu II.

The level populations of the plasma at a user-input electron temperature and density are computed using the ATOMIC code [30,31]. We perform multi-element local thermodynamic equilibrium (LTE)

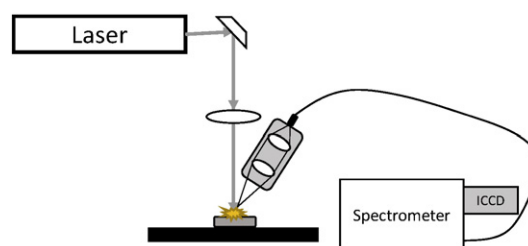


Fig. 1. Schematic of the LIBS experimental setup.

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