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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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 588.9 nm, Na I 589.59 nm, Mg I 277.98 nm, and Mg II 279.077 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 towards more neutral states, providing an explanation for the observed matrix effects found in this, and many previous, studies.

Keywords: Matrix effects, LIBS, theoretical modeling of laser induced plasma, electron density

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 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 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 1.53x 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:Cd). 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 I. The chemicals used were sodium carbonate (Na_2CO_3 , Sigma Aldrich), copper oxide (CuO , Sigma Aldrich), magnesium hydroxide ($\text{Mg}(\text{OH})_2$, Sigma Aldrich), and stearic acid ($\text{C}_{17}\text{H}_{35}\text{CO}_2\text{H}$, 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 grams. 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 minutes then pressed into 1 inch discs for 10 minutes at 34,000 lbs.

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

Table 1. Sample description including mass (grams), moles and Na/Cu or Mg/Cu ratio are shown.

2.2 Instrumentation

The LIBS experiments were carried out by using a Nd:YAG laser (CFR 400 Quantel USA) with a maximum output of 400 mJ per pulse at 1064nm operating at a repetition rate of 20 Hz (shots per second) and a pulse width of 7 ns. The delay time was varied between 0.5 and 5 microseconds 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 5Hz was used for the Mg:Cu experiments. **The focal spot diameter is approximately 350 microns and the laser pulse duration is 8 ns, which implies a laser irradiance of approximately 6×10^9 W/cm².** As shown in Figure 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 inches 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.

Figure 1. Schematic of the LIBS experimental setup.

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 **photo** ionization 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) calculations in a similar manner to previous calculations on Basalt [23]. Considering all elemental species within a self-consistent calculation is important in assessing the matrix effects observed when additional species are added to the LIBS plasma. We also accounted for the presence of the stearic acid binder and of the other possible plasma components (arising from either the carbonate, hydroxide, or oxide remnants). This was accomplished by assuming that all molecular species are fully dissociated in the plasma, and that the relative abundances in the generated plasma will be identical to the relative abundances in the target. While both of these assumptions cannot be easily tested, our focus in this study is primarily on the effects of systematically adding one component (Cu) to the emission of the Na or Mg already present in the plasma. We expect that the effects of the remaining plasma constituents (C, O, or H) will play a minor role on the emission spectra in the small wavelength range under investigation. At the temperatures considered in this study, we indeed find that more than 99% of the C, O, and H plasma components are in their neutral stage, and so make a small contribution to the global electron density. In the modeling presented in this paper, we also assume that the mass ablated by the laser is the same for each set of measurements, and that the plasma temperature is the same in each set of measurements. Without hydrodynamic modeling, beyond our capabilities at present, these appear to be reasonable assumptions. In all our calculations we include line broadening due to electron collisions based on the approach of Dimitrijevic [32], following our recent work by Johns [24].

The plasma temperature and density were iterated in the ATOMIC calculations to find the best fit to the experimental data. In particular, these conditions are constrained by the relative intensities of the lines shown in this study. In order to isolate the potential effects due to changing electron density of the plasma, we restricted our calculations to a single plasma zone at a constant temperature and mass density. Although it is likely that the real plasma is inhomogeneous and may consist of several regions at differing plasma temperature and densities, the aim of our theoretical modeling is to explore the effect of a changing electron density caused by addition of a new species to the plasma. Consideration of more than one plasma zone would obscure this effect.

3. Results and Discussion

3.1 Sodium Signal Enhancement in the Presence of Copper

A series of sodium and copper samples were analyzed to determine the role that copper plays on the signal intensity of sodium. Sodium has two main neutral (Na I) emission lines, a doublet, in the visible region of the electromagnetic spectrum that are most commonly observed in LIBS spectra: 588.99 nm and 589.59 nm. The LIBS spectra for the four samples (Na only, 1:1, 1:3, and 1:9 Na:Cu) are shown in the top panel of Figure 2. These results correspond to a delay time of 500 ns. Theoretical calculations of the sodium and copper samples are shown in the bottom panel of Figure 2, and are in very good agreement with the measured data. The calculations, which were all made assuming LTE, find that the ratio of the Na I 588.99 to 589.59 nm lines is 2:1 in all cases, which simply reflects the ratio of statistical weights of the upper levels ($3p^2P_{3/2}$ and $3p^2P_{1/2}$) that give rise to these transitions. The measurements show that this ratio is approximately 2:1 for the pure Na case, but decreases slightly for the 1:9 Na:Cu case, which may indicate that weak self-absorption effects contribute in this case.

To illustrate the increase in sodium emission intensity in the presence of copper, the enhancement factor was calculated for both the measured spectra and the theoretical calculation. For each sodium-copper mixture, the Na I 588.99 nm and 589.59 nm intensities were measured (delay time of 500 ns) and normalized to the corresponding intensity for the sodium without copper sample. The results are presented in Table 2 with a comparison to the theoretical calculation of the enhancement factor. The percent difference was calculated $[(\text{measured} - \text{theoretical}) / (\text{average of measured plus theoretical}) \times 100]$ to provide a measure of the difference in the values. A maximum enhancement factor for the Na I 588.99 nm and 589.59 nm emission lines in the measured 1:9 mole ratio were 1.76 and 1.98, respectively. Diwakar [21] reported a maximum enhancement factor of 1.53 at 15 μ s delay for the 1:9 mass ratio of sodium to copper in an aerosolized mixture. The enhancement factor was also measured for a series of delay times and can be seen in Figure 3. At the shortest delay time measured, 500 ns, we observe the highest increase (enhancement factor) of Na I. The enhancement factor for a single delay time, for example 500 ns, also varies with different amounts of copper: 1:9 > 1:3 > 1:1. As the delay time increases, and the plasma cools and expands, the sodium intensity decreases and therefore the enhancement decreases. However, an interesting effect is observed at later time delays. The sodium intensity for the three samples containing copper converge and result in lower intensities than the sodium sample alone. This trend was also observed in Diwakar's work, but at much longer time delays (60 μ s). The decrease in the enhancement factor may be related to radiation transport effects. At longer time delays, the plasma will have expanded more compared to earlier times, and this expansion may increase the possibility of self-absorption of the Na emission lines.

The physical description of this observed matrix effect (sodium emission enhancement in the presence of copper) appears to be due to the increase in the electron density (N_e) contributed by the copper atoms as determined by our theoretical modeling and shown in Table 3. The increase in the electron density shifts the populations of each atom in the plasma by increasing recombination within the plasma (ions recombining with electrons). The result is an increase in the population of the neutral states compared to the singly ionized states, increasing the Na I emission. The main assumption in this calculation is that the temperature remains the same for the four different samples.

We note that our study has focused on only one contribution to the ‘matrix effect’ phenomenon. Other factors may also influence the change in line intensities observed when different materials are added to a target. For example, it is possible that the change in target species could affect the screening of the target by the plasma. This could potentially reduce the coupling of laser energy to the sample and thus change the plasma conditions and resulting emission intensities. However, comparable measurements of ablation craters and being well below the critical electron density for plasma shielding, suggests that plasma shielding/screening is probably unimportant in the measurements reported here [8]. Also, our studies were performed in an effort to minimize such possibilities, by in particular using targets with the same total mass, as shown in Table 1. Inhomogeneities in the plasma also have the potential to obscure the origin of matrix effects. We do not consider such inhomogeneities in our theoretical modeling so that we can isolate the important role played by the electron density in the plasma.

Diwakar [21] and Hohreiter [33] both have studied laser induced plasmas of fine particles generated in the gas phase. They have determined that the difference in spectral response of these aerosolized particles (on the order of 100 nm in diameter) are due to the localized plasma environment and not the global plasma. The localized plasma environment, as they describe, will have different excitation temperatures and electron densities that can be affected by a mass composition change in the aerosolized sample [21].

There is also a large difference in laser pulse energy between LIBS analysis of aerosolized particles and the measurements reported here on bulk pressed powders: 260 mJ/pulse versus 34 mJ/pulse. The use of such high laser powers to generate a LIBS plasma will result in higher background continuum and may require longer delay times to observe the matrix effect. This will most likely affect the direct comparison of time delay studies between the aerosolized particles and bulk samples.

One complication in our analysis arises from the line widths of the measured Na lines shown in figure 2. We see that the widths of the measured lines are very similar to each other, and in fact the line widths for the Na-only measurement is slightly larger than the line width for the Na:Cu 1:9 measurement. This is in apparent contradiction with our hypothesis that the increase in line intensity is due to an increase in electron density, since the line width should be directly proportional to the electron density [24]. We estimate that the resolving power of the DEMON spectrometer provides about half of the measured line width. We think that this paradox may be due to radiation transport effects on the Na emission lines. The strong resonant Na emission lines may suffer attenuation in their transport through the plasma. Such effects may obscure the true line width of these lines.

To properly study the matrix effects caused by the addition of another species to the plasma, it would be preferable to examine non-resonant lines that are much less likely to be attenuated (since such lines are usually optically thin). Unfortunately, no such prominent lines exist for Na. However, non-resonant lines are observable from Mg, and so in the next section we turn to studies of Mg samples as well as Mg samples in the presence of Cu.

Figure 2. *Top Panel*: LIBS spectra of the sodium doublet of the four samples that vary in the amount of copper present as indicated. These results were taken with a 500ns delay. *Bottom Panel*: Theoretical calculations of the same spectra with a plasma temperature of 0.6eV and a plasma density of 3.10^{-5} g/cm^3 .

	<i>Na I 588.99 nm</i>			<i>Na I 589.59 nm</i>		
	Measured	Theoretical	% Difference	Measured	Theoretical	% Difference
1:1 Na:Cu	1.23	1.16	5.5	1.24	1.16	6.3
1:3 Na:Cu	1.49	1.37	8.0	1.55	1.38	12.0
1:9 Na:Cu	1.76	1.68	4.7	1.98	1.68	16.4

Table 2. Enhancement factor of the Na I emission lines 588.99 nm and 589.59 nm at a delay of 500 ns in the presence of copper, normalized to the intensity of the pure sodium sample emission lines. The measured results are compared to the theoretical calculation and the percent difference for each emission line is presented.

Figure 3. Sodium enhancement factor (588.99 nm) as a function of delay time for 1:1, 1:3 and 1:9 mole ratio sodium-copper pressed powders.

Sample	Ne* (cm ⁻³)
Na Only	1.3 x 10 ¹⁶
1:1 Na:Cu	1.6 x 10 ¹⁶
1:3 Na:Cu	2.1 x 10 ¹⁶
1:9 Na:Cu	3.2 x 10 ¹⁶

*For the fixed temperature of 0.6 eV and fixed mass density of the targets.

Table 3. Electron density (Ne) as a function of copper present.

3.2 Magnesium Signal Enhancement and Reduction in the Presence of Copper

A series of magnesium and copper samples were analyzed to determine the role that copper plays on the signal intensity of magnesium. Magnesium has several emission lines (Mg I and Mg II) that fall within the 275 – 286 nm spectral range as shown in Table 4. In laser induced plasmas, self-absorption, where the plasma absorbs its own emission [7], readily occurs for resonance lines associated with the ground state. This results in those emission lines being optically thick, requiring radiation transport treatment for accurate theoretical modeling. Because this has the potential to obscure any matrix effects and complicate the resulting analysis, the resonance lines Mg II and Mg I at 280.270 nm and 285.213 nm were not used in this study. Weaker magnesium emission lines that arise from transitions between levels arising from excited configurations as listed in Table 4, which are optically thin, were used instead. We note in passing that the quintet of Mg I lines from 277.5 to 278.5 nm all arise from level-to-level transitions from the same excited configurations. Two of these transitions occur at an almost identical wavelength (277.983 nm), resulting in the relatively more intense central feature observed in figure 4.

The DEMON spectrometer acquires smaller spectral windows (1-2 nm) than medium or low resolving spectrometers in order to obtain higher spectral resolution images. Therefore, the Mg I emission lines (centered at 277.98 nm) and the Mg II emission line (centered at 279.08 nm) were acquired separately and then combined, as shown in Figure 4. The top, middle, and bottom panels of Figure 4 show the experimental and theoretical comparison of Mg I and Mg II LIBS spectra for Mg only, 1:3 Mg:Cu, and 1:9 Mg:Cu, respectively. A higher temperature (compared to the Na comparisons) was required in the ATOMIC calculations to best match the measured data, which is likely due to the increased laser energy used in the Mg/Cu measurements. The increase in the electron density (N_e) from copper in the magnesium samples also promotes recombination. The interesting observation for this sample set is the transfer in population from Mg II to Mg I that results in an increase in the Mg I signal and a decrease in the Mg II signal. The same phenomenon occurs in the sodium case, but since Na II lines are not observed in a laser induced plasma, there is nothing to "decrease". Table 5 shows the ratio of Mg I 277.98 nm / Mg II 279.08nm (peak height) as a function of increasing copper for both experimental and theoretical calculations. The percent difference $[(\text{measured} - \text{theoretical})/(\text{average of measured plus theoretical}) \times 100]$ is also calculated. The larger percent difference compared to the sodium comparisons may be a result of several factors. Firstly, the need to acquire the experimental results in two different measurements as discussed above may introduce more error in the ratio comparison. Secondly, the broad Mg II line is only matched in peak height in the theoretical calculations. The line broadening predicted from the ATOMIC calculation significantly underestimates the measured line width of the Mg II 279.08nm line at the plasma density used in our calculations. We also considered the possibility that the plasma could be at larger densities that would result in increased broadening of the Mg II line; however such calculations then produced Mg I lines that were broader than the measured Mg I lines. We had to assume the same plasma temperature to fit both Mg I and Mg II spectra simultaneously. **This assumption may be the reason for the poor fit of the Mg II line width. It is possible that this measured emission line may also include contributions from regions of the plasma at different conditions than those inferred for the Mg I lines, resulting in a broader measured line.** Nevertheless, the trend of increasing Mg I and decreasing Mg II is captured in both the experimental and theoretical calculations as shown by an increase in the Mg I/Mg II ratio as the copper content increases, Table 5.

In figure 5 we present the measured Mg emission lines from the pure Mg and 1:9 Mg:Cu experiments. We see that for these (non-resonant) lines, the emission lines from the 1:9 Mg:Cu measurement are clearly wider than the emission lines from the pure Mg case. This indicates that the electron density of the 1:9 Mg:Cu plasma is indeed larger than that of the pure Mg plasma, supporting our hypothesis that the change in line intensity when Cu is added to the sample is due to the increase in global electron density of the plasma.

Magnesium Emission Lines Neutral (I) or Ionic (II)	Wavelength (nm)	E_i (cm ⁻¹)	E_k (cm ⁻¹)	Lower Level	Upper Level
Mg I	277.669	21870	57873	3P_1	3P_2
Mg I	277.827	21850	57833	3P_0	3P_1
Mg I	277.983	21870	57833	3P_1	3P_1
Mg I	277.983	21911	57874	3P_2	3P_2
Mg I	278.142	21870	57812	3P_1	3P_0
Mg I	278.297	21911	57833	3P_2	3P_1
Mg II	279.078	35669	71491	$3p\ ^2P_{1/2}$	$3d\ ^2D_{3/2}$

Table 4. Atomic parameters for the Mg I and Mg II emission lines shown in figure 4 [28]. The Mg I upper levels arise from the $3p^2$ configuration and the lower levels from the $3s3p$ configuration.

Figure 4. LIBS experimental spectra (500 ns delay) and theoretical calculations for three samples containing varying amounts (moles) of copper. Theoretical calculations consists of a plasma temperature of 0.73eV and a plasma mass density of 3.10^{-6} g/cm³. *Top Panel:* The results of magnesium only experimental versus theoretical. *Middle Panel:* The results of the 1:3 magnesium to copper mole ratio experimental versus theoretical. *Bottom Panel:* The results of the 1:9 magnesium to copper mole ratio experimental versus theoretical.

Mg I 277.98 nm / Mg II 279.08 nm		
Measured	Theoretical	% Difference

Mg Only	0.98	1.41	-36.35
1:3 Mg:Cu	2.02	1.54	26.52
1:9 Mg:Cu	2.08	1.87	10.44

Table 5. Mg I/Mg II ratio as a function of copper for both experimental measurements and theoretical calculations are shown. Percent differences were also calculated and are reported in the last column of the table.

Figure 5. LIBS experimental spectra (500 ns delay) of the pure Mg (black line) and 1:9 Mg:Cu (green line) samples.

4. Conclusion

In this manuscript, pressed powders varying in sodium, magnesium and copper content were analyzed using LIBS to determine the role that copper plays on the emission intensity of sodium and magnesium. The results showed that the amount of copper (as a ‘matrix element’) significantly impacts the intensity of the analyte, either increasing or decreasing the emission intensity as shown in the magnesium study for

Mg I and Mg II, respectively. The presence of copper appears to increase the electron density of the plasma, causing an increase in recombination. The result is a shift of the singly ionized ion populations to the neutral atom states. This was observed spectrally as an increase in the Na I and Mg I emission intensity and a decrease in the Mg II intensity. This experimental result was supported by our theoretical modeling. **Although an increase in plasma electron density should also lead to an increase in emission line widths, this was observed only for the Mg (non-resonant) lines, but not for the Na (resonant) lines. We attribute this to possible radiation transport effects on the Na lines, which may lead to line attenuation, distorting the line widths.** Furthermore, different delay times also result in a varying degree of enhancement as the plasma cools. When copper was present, the Na I emission dropped below that of the Na I without copper present at longer delays (>2 s). These results illustrate how relatively small changes in elemental composition can significantly change the excited state populations and resulting spectra. Binary mixtures, such as the examples presented here, are much easier to model, especially when the emission spectra are simple (several emission lines compared to many hundreds). Including the contribution from all the elements in the ablated sample to the electron density of the laser induced plasma will result in more accurate determinations of elemental composition. More work in this area is anticipated.

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