

Feedstock Quality Factor Calibration and Data Model Development

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Objective:

The goal of the feedstock assembly operation is to deliver uniform, quality-assured feedstock materials that will enhance downstream system performance by avoiding problems in the conversion equipment. In order to achieve this goal, there is a need for rapid screening tools and methodologies for assessing the thermochemical quality characteristics of biomass feedstock through the assembly process. Laser-induced breakdown spectroscopy (LIBS) has been identified as potential technique that could allow rapid elemental analyses of the inorganic content of biomass feedstocks; and consequently, would complement the carbohydrate data provided by near-infrared spectrometry (NIRS). These constituents, including Si, K, Ca, Na, S, P, Cl, Mg, Fe and Al, create a number of downstream problems in thermochemical processes. In particular, they reduce the energy content of the feedstock, influence reaction pathways, contribute to fouling and corrosion within systems, poison catalysts, and impact waste streams.

Expected Outcome:

The mineral content and composition is recognized as both a barrier to the use of some feedstocks and as a quality attribute that may be controlled through the feedstock assembly process. The inorganic content of biomass feedstocks is known to vary over wide ranges, depending upon the plant type and anatomical fraction, growing conditions, harvesting time and method, and handling operations. If this task is successful in developing a cost-effective screening tool, there may be opportunities for selecting and blending diverse feedstocks to produce on-spec materials that will in turn, reduce the capital and maintenance costs associated with syngas cleaning and replacing components in conversion platforms.

Progress:

Scoping studies have been conducted with the instrumentation in order to establish the feasibility of using the LIBS technique as a feedstock screening tool and to determine the optimal system operational parameters. These parameters include identifying the most sensitive, interference-free analytical lines for key elements and the laser ablation pulse parameters for sampling the materials. The sensitivity of the analytical lines to changes in elemental concentrations over ranges of interest has been benchmarked against independent analytical analyses conducted by Hazen Research Inc. (Golden, CO).

Introduction:

LIBS is a technique that is similar, in principle, to atomic emission spectroscopy (AES) which uses an electrode to produce a plasma. In AES, solutions (created from acid digested feedstock materials) are introduced into the plasma where they are vaporized, and the resulting atoms and ions are electronically excited. Each element present emits light at a characteristic wavelength, which is spectrally resolved to identify the elemental species. As illustrated in Figure 1, in LIBS, a high-energy laser pulse is focused on a sample producing a high-temperature (approximately 10,000 K) plasma in which a small amount of

sample material is reduced to elemental constituents which are electronically excited to form single- and multiple-charged ions. Light from the plasma is collected and focused onto a spectrometer and analyzed by a gated detector, in this case an intensified charge couple device (ICCD). Since the atoms making up the various elements have different energy states with different transition probabilities, a number of spectral lines are produced that can be used to uniquely identify elements in the sample. The sensitivity of a line depends upon the probability of an electron making a particular transition that produces light at that wavelength, and the most probable transitions result in the most intense spectral lines. Quantitative analysis of elements of interest is performed by comparing the intensity of characteristic spectral lines with similar lines obtained from samples of known composition.

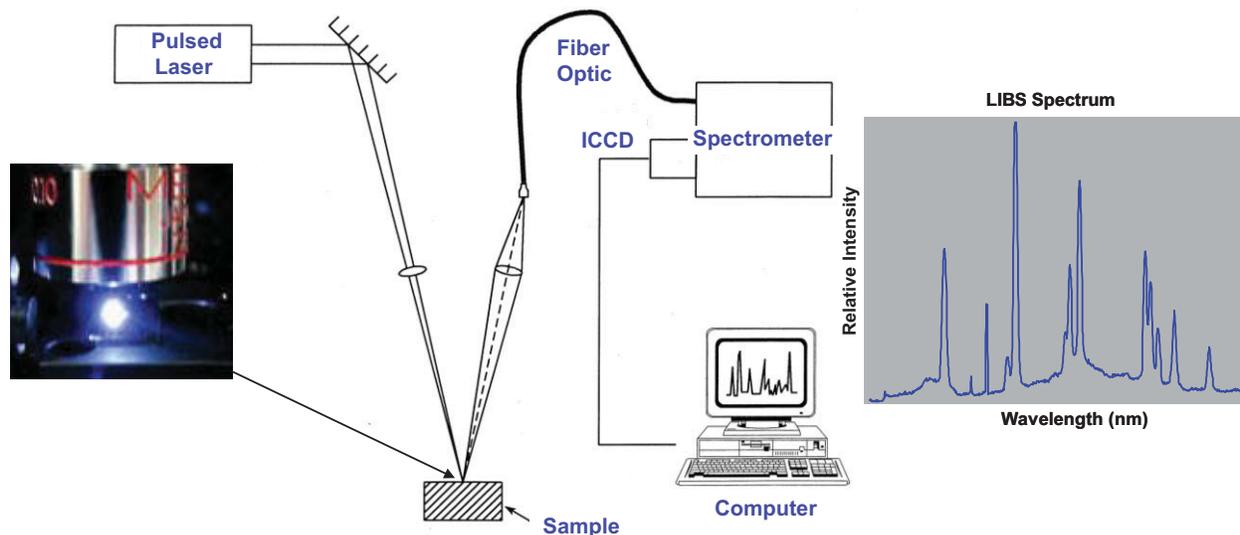


Figure 1. Laser-Induced Breakdown Spectroscopy (LIBS) Measurement

Recent years have witnessed considerable activity employing LIBS to characterize numerous materials [1, 2, 3, 4]; however, very few applications have involved biological materials. Sun et al. [5] used NIST certified reference materials and mixtures of these materials to construct LIBS calibration curves, which were employed with LIBS analysis to determine the concentration of Ca, Mg, P, Fe, Cu, Mn, Zn, and Al in plant leaves. It was found that a gate delay of 1 μs and an integration time of 10 μs provided the optimum signal to noise ratio and that the coefficient of variation of measurements was approximately 8-15%. Cho et al. [6] mixed starch powder or NIES samples with 50% (w/w) to improve sample rigidity for optimal plasma formation and used the Mg line at 279.553 nm and the K line at 766.49 nm to determine concentrations of those elements with detection limits of 0.4 and 3 $\mu\text{g/g}$ for Mg and K, respectively.

Kaiser et al. [7] compared femtosecond LIBS with X-ray radiography for spatially resolving Cd and Pb in leaves and roots, although quantitative results were not obtained because standard reference samples were not obtained. Similarly, Samek et al [8] demonstrated the utility of femtosecond LIBS to image Fe accumulation in leaf veins and nearby leaf material with high spatial resolution and sensitivity. Gornushkin et al [9] investigated the influence of the matrix on Mg signals in powdered samples, and proposed a surface density normalization method to compensate matrix effects that are problematic for quantitative elemental analysis. Gornushkin et al. noted that the Mg II weak lines at 292.78 and 283.65 nm were observable and could be used for quantitative analysis at concentrations above 0.7%. For samples with very low concentrations (even below 0.001%), the strong ionic lines at 279.806 and 280.27 nm and the atomic line at 285.213 nm can be used. However, these strong lines experience substantial self-absorption at concentrations approaching 0.5%, which limits their range of linear dynamic response.

More recently, Nunes et al. [10] optimized LIBS parameters and validated the LIBS approach for the determination of macronutrients P, K, Ca, and Mg and micronutrients B, Cu, Fe, Mn, and Zn in pelletized

sugar cane leaves. Quantitative determinations were performed using univariate calibration and chemometric methods on a total of 26 laboratory reference samples to construct calibration curves and an additional 15 test samples to validate the method. The samples were also microwave-assisted digested and analyzed by ICP OES for comparison. Repeatability precision of measurements obtained by univariate and multivariate calibrations ranged from 1.3 to 29% and 0.7 to 15%, respectively, demonstrating that LIBS is a powerful tool for analysis of plant pelletized material.

The above-referenced studies provide a framework for employing LIBS to determine concentrations of both macro- and micro-nutrients in several plant materials. However, a considerable amount of work remains to be completed before LIBS can be used for rapid screening of the inorganic content (Si, K, Ca, Na, S, P, Cl, Mg, Fe, and Al) of biomass feedstocks to mitigate problems that such species create in thermochemical processes. Specifically, not only must reference standards be constructed to accurately represent the various feedstock material matrices, but sampling protocols must be designed to account for equipment and material variances, such as occur in nanosecond laser pulse production, plasma spark forma, and in feedstock composition and microstructure. This work is dedicated to advancing these objectives.

The advantages of LIBS are that it can be used to perform rapid, in situ, multi-element analysis of samples and requires very little or no sample preparation, which minimizes the risk of sample contamination and avoids waste streams. It is minimally-evasive and allows for high spatial resolution measurements (important in looking at tissue fractions). It can be designed as user-friendly, field-portable units (systems have been designed for deployment on the Mars Rover). In contrast, competing techniques, such as inductively coupled plasma optical emission spectrometry (ICP-OES) [11,12], inductively coupled plasma mass spectrometry (ICP-MS) [13] and flame atomic absorption spectrometry (FAAS) [14] require that samples be dissolved, which is expensive in time and/or reagents.

The LIBS system (RT-100HP, Applied Spectra, Inc. Fremont, CA) used in these studies was obtained contains a Nd:YAG laser that emits at 1064 nm with a 10 mJ, 5 ns pulse. The laser output is focused to spot of approximately 0.5 mm on the sample. The sample is placed on a stage that can be accurately moved in three dimensions for interrogating the sample. There is also a color camera and visible (red) alignment laser to assist in the alignment of the sample in the instrument. The plasma light is collected by a lens and focused via an optical fiber cable onto a dual grating Czerny Turner spectrometer equipped with a high resolution (2400 l/mm) and a lower resolution (600 l/mm) grating. The signal is then detected by an intensified CCD detector with extended infrared response to enhance the possible of line detection in the near infrared.

Key Results:

As noted above, a number of variables influence plasma formation, and hence LIBS signal production, and can skew quantitative results. These variables include such parameters as laser pulse energy, pulse duration, and the focusing laser spot size, which must produce sufficient power density to breakdown the material. In addition, physical and chemical properties of the sample, such as thermal conductivity, specific heat, and microscale homogeneity affect plasma formation and are known as matrix effects. These effects are particularly strong in biomass feedstock materials because microscale inhomogeneities inherent in such materials introduce substantial variability in plasma formation.

Because LIB spectra are sensitive to numerous parameters that can vary during experiments, it is necessary to record multiple spectra and average the results to obtain representative spectra. Spectra should be averaged not only from multiple sample locations to account for material inhomogeneity (physical or structural as well as chemical) but also from multiple spectra collected from the same location. Figure 2a contains spectra from a burst of 10 laser pulses on a #60 grind corn stover pellet (compressed at approximately 5000 psi for one minute). Notably, the first spectrum is substantially different than subsequent recordings. This is typical of spectra collected from sequential laser bursts and

is due primarily to the effects of the sample's morphology on plasma formation. Before the first laser pulse, the sample surface is nearly flat but each laser pulse removes material and essentially digs a hole that becomes deeper with each laser pulse. Thus, each laser pulse changes the sample morphology, which effects the plasma formation of subsequent laser experiments.

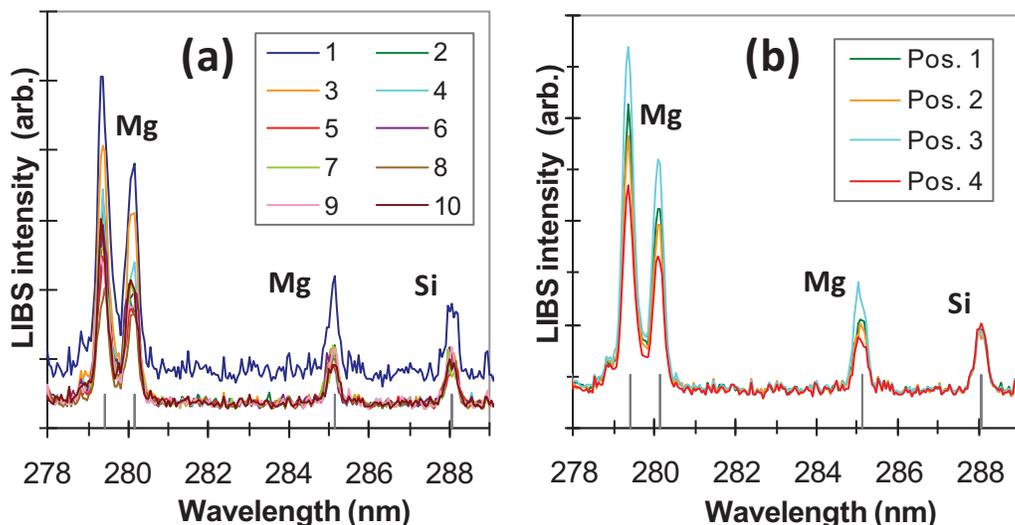


Figure 2. LIB spectra from corn stover (#60 grind) showing peaks due to magnesium and silicon. (a), Spectra from a burst of 10 laser pulses from a single sample location. Green curve in (b) is the average of spectra 4 through 10 from (a). Other curves in (b) are similarly averaged spectra from other sample locations. Gate delay = 1.5 μ s; Gate width = 3 μ s; Gain = 160.

To minimize variation in quantitative predictions, LIB spectra are collected during bursts of 10 laser pulses, and spectra obtained from first one or two laser pulses are rejected from the averaging process. Other spectra that are substantially different from the remaining spectra are also rejected from the averaging process (dramatic differences can be caused by several factors such as the collapse of the hole in the sample dug by the laser or the presence of large anisotropic particles in the laser path). Even after outlier spectra are rejected, considerable variation exists in spectra collected from different locations, as illustrated in Figure 2b, which exhibits the average of spectra collected from four different positions on the same corn stover pellet featured in Fig. 2a. Interestingly, the intensity variation is much greater for the magnesium peaks than for the silicon peak, which may be due to inhomogeneous distribution of magnesium within the sample. Accurate quantitative elemental analysis will require that the source of the variation in the LIBS signal be identified and properly compensated using an internal standard. An effort is underway to identify naturally occurring internal standards in the LIBS spectra (an element with an observable LIB spectra that occurs in either the same or known concentrations for all specimens) as well as to introduce non-natural internal standards by mixing known quantities of elemental powders such as germanium into feedstock powders.

The small Si and Mg peaks in Fig. 2 also illustrate the challenge of distinguishing small peaks in LIBS spectra from background noise, which is crucial for measuring concentrations of trace analytes. Timing or gating the collection of the signal can greatly improve the detection sensitivity by filtering background (continuum) radiation that is produced by collisions between free electrons and excited atoms and ions in hot and dense plasmas. In addition to background radiation, which can bury or obscure elemental emission, self-absorption within the plasma can also block elemental emission and significantly reduce the LIBS signal intensity. Consequently, timing or gating the collection of the signal can greatly improve the detection sensitivity as illustrated in Fig. 3 and Table 1, which contain LIBS data obtained from apple

leaf powder (NIST standard 1515). The experimental parameters were the same for all four spectra exhibited in Fig. 3, except for the gate delay time, which was varied from 0.5 to 4 μ s. Each of the spectra in Fig. 3 represents the average of approximately 10 spectra as described above. Notice that increasing the delay time substantially reduces both the background noise and the overlap between nearby spectral peaks. For example, the aluminum peaks centered at 394.4 nm and 396.2 nm are completely dominated by the nearby calcium peaks for gate delay times less than approximately 2 μ s.

The gate delay time also greatly affects the signal to noise (S/N) ratio, which was calculated for each peak by dividing the net signal intensity by the estimated background noise. The net signal intensity was obtained for each LIBS peak by subtracting the local background noise, which was estimated using standard least-squares regression to fit linear curves to several data points lying on each side of the LIBS peak. Care was taken to ensure that selected data points were as close as possible to the LIBS peaks while being truly representative of the local background noise with minimal influence from other spectral peaks. At least 20 data points were selected cumulatively from both sides, and the background noise was estimated by calculating the standard deviation of the selected data points from the corresponding least-squares linear fit. The results of the S/N analysis for the key inorganic elements featured in Fig. 3 are documented in Table 1. Notably, for the Mg peaks, the greatest S/N ratios are obtained with short gate delay times, whereas much longer gate delay times are necessary for the Ca and Al peaks because the very strong Ca peaks saturate the detector and bury the Al peaks for short gate delay times.

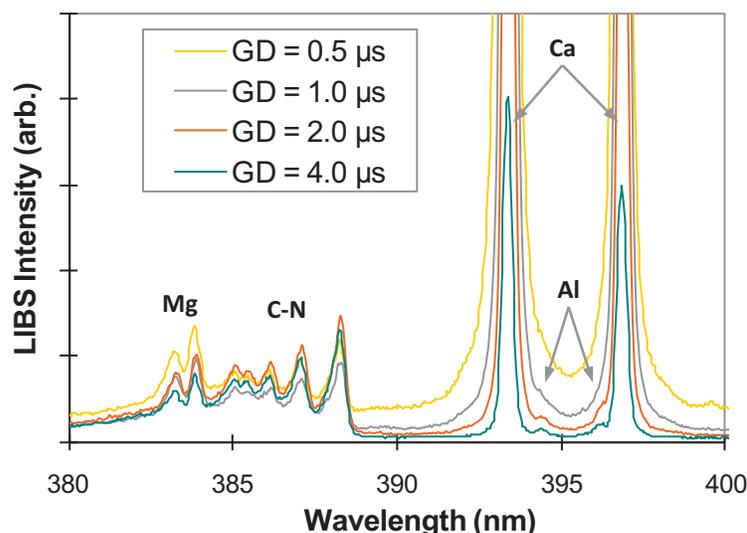


Figure 3. LIB spectra from NIST 1515 apple leaves grind showing peaks due to Mg, C, N, Ca, and Al for gate delay (GD) times of 0.5, 1.0, 2.0, and 4.0 μ s. Gate width = 3 μ s; Gain = 200.

Table 1. S/N Ratio for Peaks of Key Inorganic Species in Fig. 3

Peak (nm)	Element	GD = 0.5 μ s	GD = 1.0 μ s	GD = 2.0 μ s	GD = 4.0 μ s
383.2	Mg	49	41	21	22
383.8	Mg	63	52	29	39
393.4	Ca	^s	^s	^s	989
394.4	Al	^b	^b	52	23
396.6	Al	^b	^b	^b	9
396.9	Ca	^s	^s	^s	682

^s Peak intensity exceeded detector threshold (saturation) making S/N calculation impossible

^b Peak buried under nearby strong Ca peak

A complete list of analytical lines for key inorganic species that have been identified to date is summarized in Table 2. Some of the inorganic species, such as Cl, Fe, and S typically occur in biomass feedstocks in very low concentrations, making it difficult to observe their spectral lines with LIBS. Thus, lines that are documented in the literature but that we have not yet observed in this study are shown in gray shaded text. Similarly, we have been unable to observe some lines because of the limited wavelength range of the Czerny-Turner detector in our LIBS system, which has a ranges of approximately 150-850 nm and 250-650 nm for the coarse (600 l/mm) and fine (2400 l/mm) gratings, respectively. Spectral peaks which we have only been able to observe with the coarse grating are marked with a superscript ‘c’ in Table 2.

Table 2. LIBS Emission Peaks for Key Inorganic Species

Element	Emission Wavelength (nm)
Aluminum	257.5, 308.2, 309.3, 394.4 ^m , 396.2
Calcium	315.9, 317.9, 364.4, 370.6, 393.4, 396.9, 422.7, 430.8, 443.5, 445.5
Chlorine	479.5, 543.3, 837.6 ^c , 858.6 ^c
Iron	248.3 ^m , 248.8 ^m , 302.1, 527.0
Magnesium	278.0, 279.6, 280.3, 285.2, 292.9, 293.7, 383.2, 383.8
Phosphorus	214.8 ^c , 253.6, 602.4, 650.4, 650.8
Potassium	404.8, 766.5 ^c , 769.9 ^c
Sodium	819.6 ^c ,
Silicon	251.6, 288.2
Sulfur	416.3 ^m , 543.3, 545.4

^c Only accessible with coarse 600 l/mm grid

^m Peak may include a substantial contribution from multiple elements

Shaded gray: peak documented in literature but not yet observed in this study

Calibration curves for determining the concentration of critical element constituents (Si, K, Ca, Na, S, P, Cl, Mg, Fe and Al) are being developed using the peaks listed in Table 2. In order to create the calibration curves, samples of a high ash and low ash feedstock, including corn stover (7.31%) and pine wood without bark (0.27%) were sent to an established analytical laboratory (Hazen Research, Inc.) for independent elemental ash analysis. Replicates of these samples were ground through a 60 mesh screen and then pelletized by compressing the material in a die at a pressure of approximately 5200 psi for one minute. Figure 4a compares averaged LIB spectra obtained from #60 ground and pelletized corn stover, switch grass, and pine wood in the wavelength range 392-398 nm, which includes calcium and aluminum peaks. 10 spectra were obtained at each of three locations on each sample and averaged as described above to form the curves exhibited in Fig. 4a. The net intensity of each peak was estimated by subtracting the background noise as discussed previously and is plotted in Figures 4b and 4c as a function of analytical concentration (obtained from Hazen Research, Inc.) for the calcium and aluminum peaks, respectively. Linear curve fits to the data are included as dashed lines, although it is obvious that scatter in the data makes it impossible to correlate LIBS peak intensity with analytical concentration with any useful degree of precision for either calcium or aluminum. A further disturbing observation for the aluminum concentration calibration data is that not only is there considerable scatter in the data, but the trend does not appear linear, indicating that matrix effects are substantial. It may possible to compensate for matrix effects by identifying an intrinsic internal standard, such as carbon, or it may be possible to introduce a foreign standard into the powder by mixing in a small but known concentration of analyte, such as a few weight percent of germanium powder. It may also be necessary to develop separate calibration curves for each feedstock and feedstock format as observed previously. Further experiments are necessary to determine the best approach. It is also worth noting that the scatter in the data observed here is significantly larger than that reported in previous studies [6, 9, 10], which may be related to the relatively weak laser pulse energy (10 mJ) employed in the present study compared to those used in other studies (100-350 mJ) [6, 9, 10]. Greater laser pulse energies consume more sample matter per laser pulse

to somewhat mitigate microscale inhomogeneities in the sample and can also benefit from more stable plasma formation.

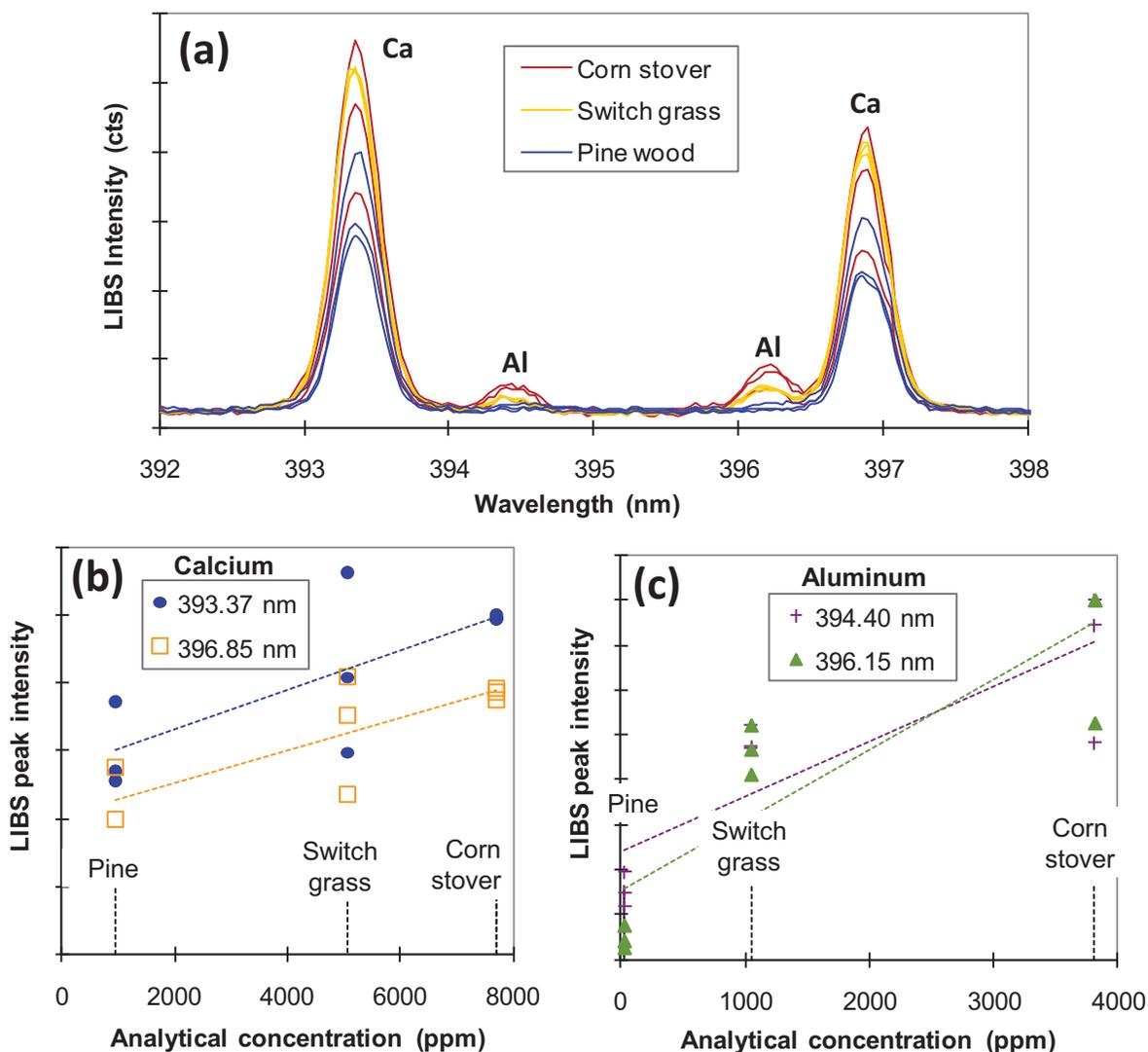


Figure 4. (a), Averaged LIB spectra from #60 ground and pelletized corn stover, switch grass, and pine wood. (b) and (c), LIBS peak intensities as functions of constituent concentration (from ICP analysis, Hazen Research, Inc.). Gate delay = 1.5 μ s; Gate width = 3 μ s; Gain = 200.

Figure 5 contains additional spectra in the wavelength range 279-289 nm obtained from the analyzed corn stover, switch grass, and pine wood samples featured in Fig. 4 and was collected and processed in a similar manner. The switch grass spectrum has been scaled by a factor of 0.1 to make it comparable to the other spectra. The switch grass spectrum has been scaled by a factor of 0.2 to make it comparable to the other spectra. Importantly, although the peaks in the switch grass spectra are much more intense than peaks in the other spectra, the corn stover sample actually has higher concentrations of both magnesium and silicon, as demonstrated in Figures 5b and 5c. Presumably, once again matrix effects are responsible for causing the switch grass spectra to be more intense than that from the corn stover. Another possibility, particularly for the strong ionic Mg peaks, is that the peaks are saturated due to high constituent concentrations and strong self-absorption [10]. To avoid this problem, Gornushkin et al. [9] recommended the use of Mg II weak lines at 292.863 and 293.651 nm; however, because of the weakness

of these lines, they can only be observed in samples with relatively high concentrations of Mg, limiting their usefulness.

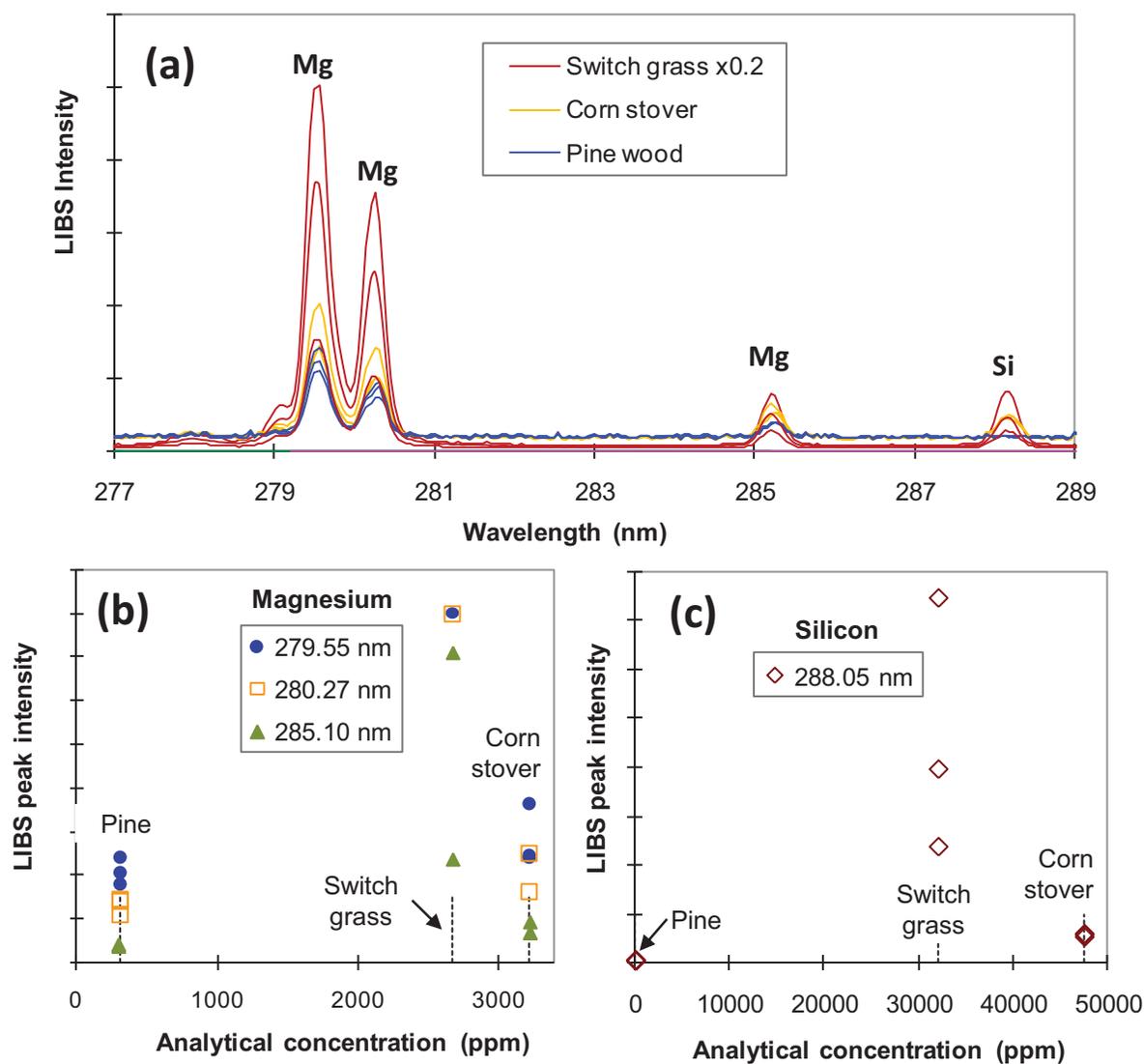


Figure 5. (a), Averaged LIB spectra from #60 ground and pelletized corn stover, switch grass, and pine wood. (b) and (c), LIBS peak intensities as functions of constituent concentration (from ICP analysis, Hazen Research, Inc.). Gate delay = 1.5 μ s; Gate width = 3 μ s; Gain = 200.

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