FEASIBILITY STUDY: LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) AS A GLASS MELT MONITOR

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Introduction

The harsh environment of molten glass makes it difficult to probe the chemistry of the glass components as the melt progresses to completion. It would be helpful to have a way to follow the melt process to help understand how the components interact and determine when it has reached completion.

We propose an experiment that could help determine the feasibility of this type of monitor. Again, this is only a feasibility study. The technique to be used is laser induced breakdown spectroscopy (LIBS).

Laser-induced breakdown spectroscopy, also referred to as laser-induced plasma spectroscopy (LIPS) or laser spark spectroscopy (LASS), dates to the 1960s[1-4]. The LIBS technique utilizes a small (typically <1 mm diameter) laser-induced plasma to dissociate all molecules and fine particles within the highly energetic plasma volume. Continuum emission (bremsstrahlung and electron-ion recombination) and atomic line emission are observed from the ensuing plasma emission. The atomic emission lines may be resolved both spectrally and temporally, enabling identification and quantification of the elements present. The LIBS technique has been applied to the analysis of solids, liquids, and gases, and a number of literature reviews are available that cover a wide range of LIBS-based analysis[5-8].

Measuring components of hot processes can be difficult due to the obvious concern of temperature effects on the apparatus use and the chemical activity of the environment. Information regarding environmental concerns, reactor life, or reaction activity can be identified through such measurements. A laser induced plasma is a reasonable choice for obtaining information from a hot, corrosive environment if the delivery and collection optics can be protected. The application of LIBS to hot environments is not new. LIBS has been applied to directly probe a lab scale glass melt at about 1600 ºC to determine glass composition as an "in-line" process monitor[9]. Later this was applied to a production scale melt[10]. Others have successfully monitored melted alloy at about 800 ºC[11]. Several applications exist that monitor dilute or dense particles from a hot exhaust and can be found reviewed elsewhere[12]. Corning, Inc. has successfully extracted the hot gases from inside a melt tank to identify trace impurities to understand tank wear mechanisms[13]. We believe it is possible to use vapor phase composition above the glass melt (a few millimeters) to understand melt progress. This information could lead to better control of the energy used to produce glass through automated feedback mechanisms.

The experimental concept is to focus the LIBS plasma above the glass melt and collect emission from the elements that are in the gas phase directly above. By following their signal over time it may be possible to predict energy needs through the course of the melt and predict when the melt is complete. The proposed experiment would involve collecting elemental emission from a LIBS signal that is focused above a glass or flux melt in a platinum crucible. The difficulties of transferring this concept to a furnace or melt tank will be reviewed.

Experimental

The overall plan of the experiments was to melt a few grams of batch material and use the LIBS instrument to monitor the changes in elemental signals above the surface as melting occurred. The LIBS instrument has been described elsewhere in complete detail,[12] so a shortened description will be presented here. A schematic of the LIBS system is seen in Figure 1.

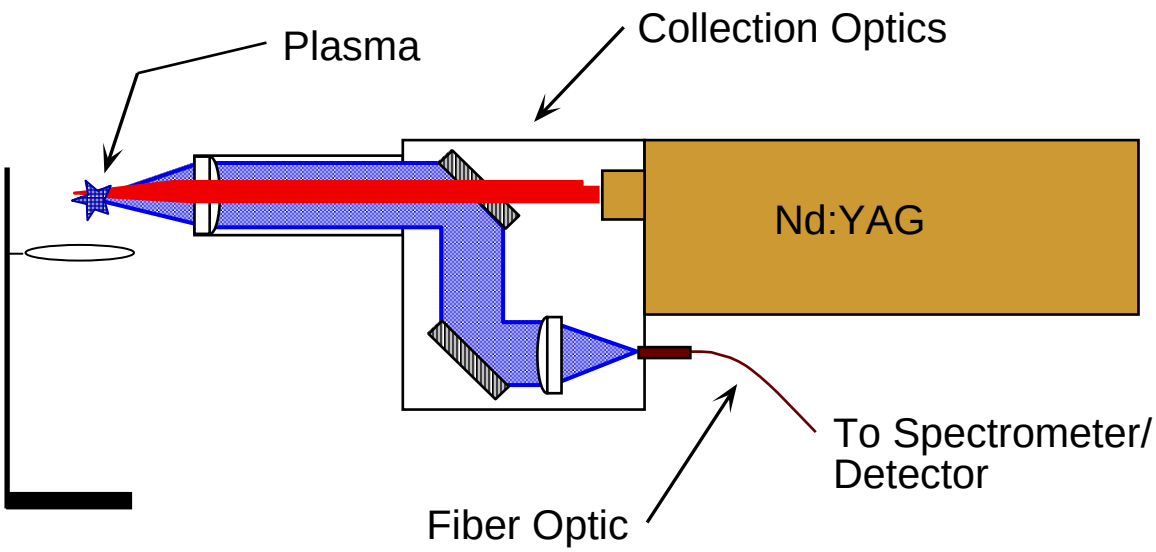

Figure 1. Schematic of the LIBS instrument and optical design, including the ringstand used to hold the sample crucible.

The output of a Q-Switched Nd:YAG laser (Quanta-Ray INDI-40-10, Spectra-Physics), in this case operating on the fundamental wavelength (1064 nm), is focused to a point.

The intense electric field of the focused laser induces electric breakdown in the air at that location. This breakdown leads to vaporization of any solid or liquid materials present, disassociation of any molecules and subsequent ionization of the liberated atoms, i.e. a plasma is produced. The plasma continues to absorb energy throughout the course of the laser pulse. Once the laser pulse ceases, the plasma begins to cool and the ionized and excited atoms fluoresce. It is this fluorescence that is collected and dispersed by the LIBS spectrometers.

The LIBS system employed a *Q*-switched Spectra-Physics Quanta-Ray INDI-40 Nd:YAG laser delivering ~200 mJ per pulse at 1064 nm with a pulse width of 10 ns. The laser repetition rate was 10 Hz. An échelle spectrometer and a Czerny-Turner spectrograph coupled with a Princeton Instruments ICCD were used in parallel to collect emission from the plasma. A 10-m-long bifurcated ultraviolet-grade fused-silica fiber optic bundle facilitated simultaneous use of two different spectrometers.

The échelle system was a Multichannel Instruments AB Mechelle 7500 échelle grating spectrometer combined with a PCO Computer Optics GmbH DiCam-PRO intensified charge-coupled device (ICCD) camera. The ICCD contained a 1280 x 1024 pixel array with a dynamic range of 12 bits/pixel. The combination of the échelle spectrometer and its ICCD provides sensitivity over a continuous range from 200 to 850 nm with a constant spectral resolution of $\lambda/\Delta\lambda = 4000$. We used the manufacturer provided software to set a delay time of 10 μs and a gate width of 15 μs for the échelle spectrometer. Spectra were collected by the ICCD at a frequency of 5 Hz. The signal from 5 laser sparks was accumulated on the ICCD prior to read out by the computer. The results from 20 such frames were merged to form one spectrum. This technique improved the signal-to-noise ratio, but decreased the temporal resolution. The ICCD was operated with a gain setting of 999 and with a channel height of 5 pixels.

The second spectrometer was composed of an Acton Research Corporation SpectraPro-275 0.275-m triple grating monochromator/spectrograph (600, 1200, and 2400 grooves/mm) coupled to a Princeton Instruments (PI) ICCD with an ultraviolet-extended 1024 x 256 array. The fiber-coupled PI system is also sensitive from 200 through 900 nm. The only grating used during these experiments had 2400 grooves/mm, giving a detection window of 35 nm and a spectral resolution greater than 0.1 nm. Typically, the PI system was situated with a spectral window centered on 277 nm to capture the lead and silicon signals. The ICCD was operated with a gain setting of 700 V and a channel height of 120 pixels. The delay time selected was 10 μs, the gate time was set at 25 μs. This system possess a much faster readout time, so each individual laser spark was recorded separately, as well as the average of every 100 laser shots.

Given the limited scope of the project, a series of simple, but effective experiments were designed. A simple experimental apparatus was constructed consisting of the LIBS instrument, a platinum crucible, a few ring stands and a propane torch, seen in Figure 2. A few grams of a generic lead glass batch was placed into the platinum crucible and heated with the propane gas torch.

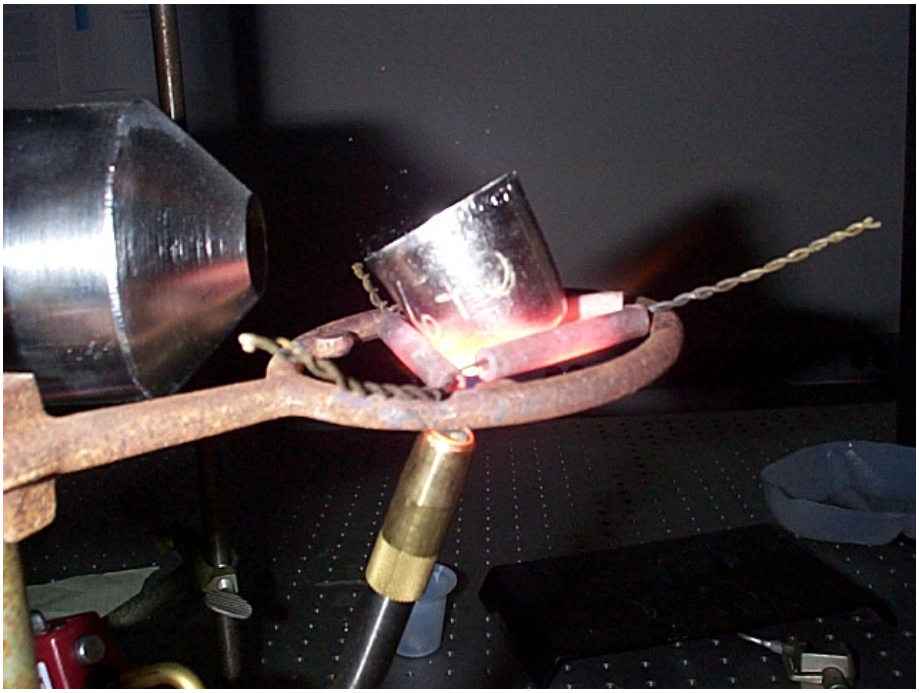

Figure2. First experimental setup using a platinum crucible. The high walls of the crucible made it difficult to position the LIBS plasma close to the melt surface.

The composition of the lead glass batch created for these experiments is described in Table I. This composition is typically manufactured at about 1400 ºC. The melting point of the batch facilitated use of the torch as the sole heat source.

Table 1. Nominal Glass Composition

Component	**%by wt**
SiO2 as Sand	54.86
Al2O3 as Alumina	0.99
Na2O as Sodium Carbonate	6.99
PbO as Litharge	27.71
BaO as Barium Carbonate	8.77
SrO as Strontium Carbonate	0.12
CaO as Calcium Carbonate	0.02
H2O	0.52
SO3	0.02

During heating of the batch the LIBS instrument was run collecting data from the batch and the consolidated melt. After a few runs with the arrangement shown in Figure 2, several shortcoming were identified in the setup. First of all, either one or two propane torches were insufficient to evenly heat the crucible. Secondly, the quantity of batch

required to generate a pile large enough to permit observation of the batch/melt surface via LIBS made the heating process less efficient as well.

These shortcomings were addressed by switching the heating source to a Mapp gas torch, (44% acetylene) and changing from a crucible to a shallow platinum boat. Mapp gas can achieve temperature as high as 2900 ºC. This setup is shown in Figure 3. The smaller quantity and lower sidewalls of the boat permitted the laser a closer interaction with the surface of the batch and glass. The typical batch size for each experiment was approximately 0.5 grams. The total melting time was approximately five minutes.

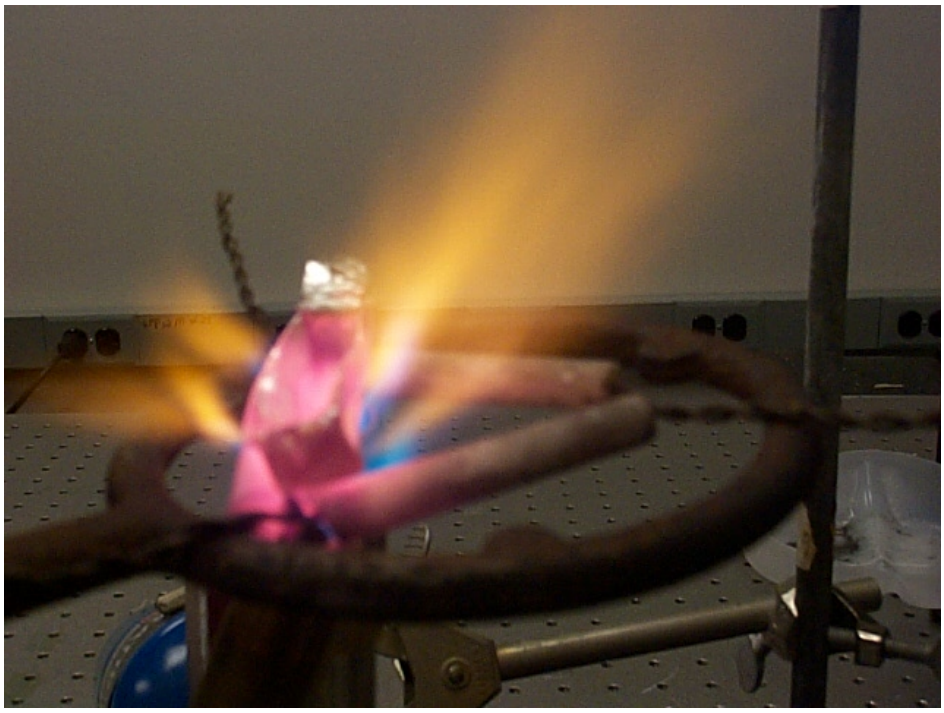

Figure 3. The second experimental configuration using a platinum boat and Mapp gas torches. The focusing/collection optic for the LIBS instrument is out of sight on the left hand side

While the closer proximity of the laser plasma to the surface of the batch increased signal intensity, it also created a different problem. The plasma formation caused a concussion in the air that was sufficient to displace the batch powder. If the laser was set to run prior to consolidation of the batch, the force of the concussion was sufficient, over the course of several seconds, to move all of the batch material away from the spark. The disturbance of the batch material did aid signal intensity since it threw batch particles into the air where they were more easily sampled by later laser sparks. The movement of the batch material, however, caused an artificial decrease in signal intensity during the course

of the melt that did not correspond to a phase or chemical change, but instead to a relocation of sample material.

The simplest solution to this problem was to not start the laser, and subsequent data collection, until after the batch had consolidated. To accomplish this, the sample was positioned, relative to the laser plasma formation, and the torches lit. Then as soon as the glass began to form, the laser and spectrometers were started. Following this modification the elemental signals were much improved in stability.

A slightly more complex experiment involved measurement of the relative vapor-phase concentration of Pb above the melt surface as a function of height. This experiment followed the same procedure for startup as the previous experiments, waiting for consolidation to before starting data collection and laser. The laser focal point was positioned at the surface of the melt for approximately 200 shots (20 seconds). Subsequent data points were collected at three different heights: 1, 3, and 5 mm above the melt surface. In all cases at least 200 shots were collected. The first set of these experiments had the PI system centered on the lead lines near 280 and 260 nm. The second run of this experiment moved the PI system to barium line at 455 nm. The third run collected the signal for the sodium doublet at 589 nm. The signal intensities for these elements as a function of height above sample can be seen in Figure 4. Sample spectra for Pb, Ba, and Na, can be seen in Figures 5, 6, and 7. These were taken from lead metal, barium nitrate and sodium nitrate respectively. This experiment allowed for conclusive identification of the analyte peaks of interest.

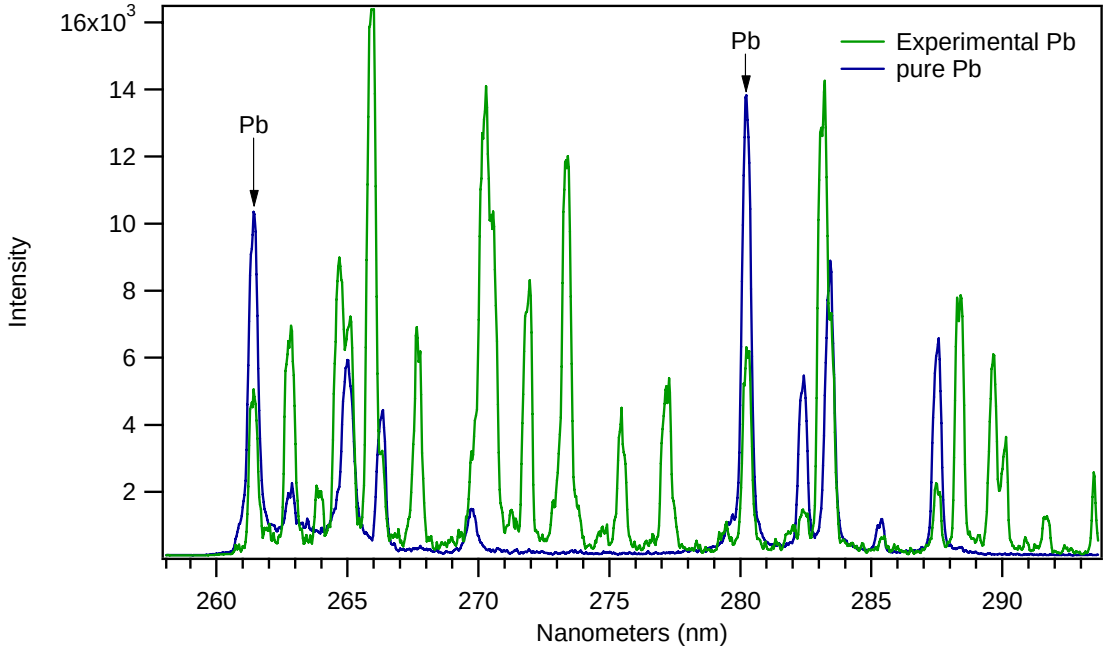

Figure 5. Spectra of lead at 260 and 280 nm collected on Princeton Instruments spectrometer system

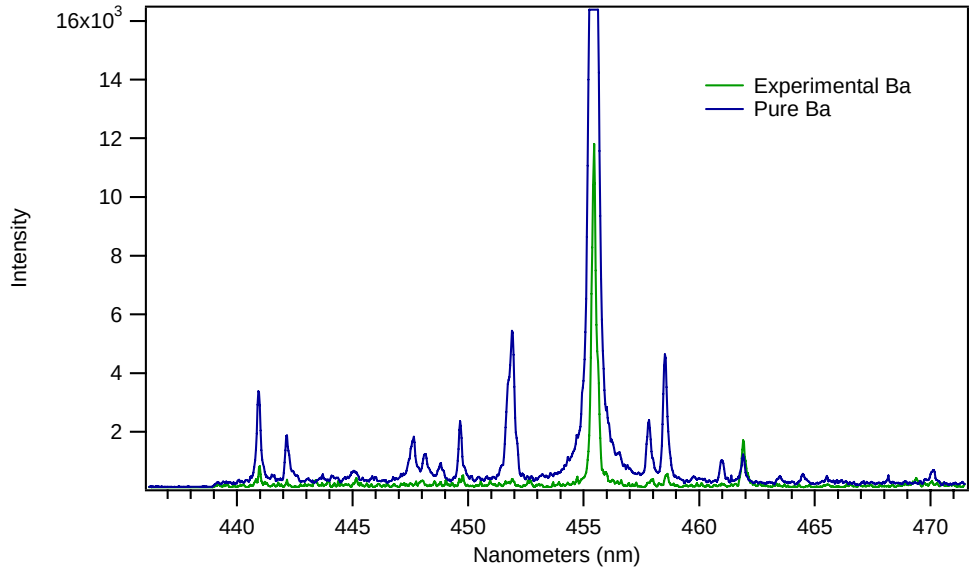

Figure 6. Spectra of barium line at 455 nm collected on Princeton Instruments (PI) spectrometer system

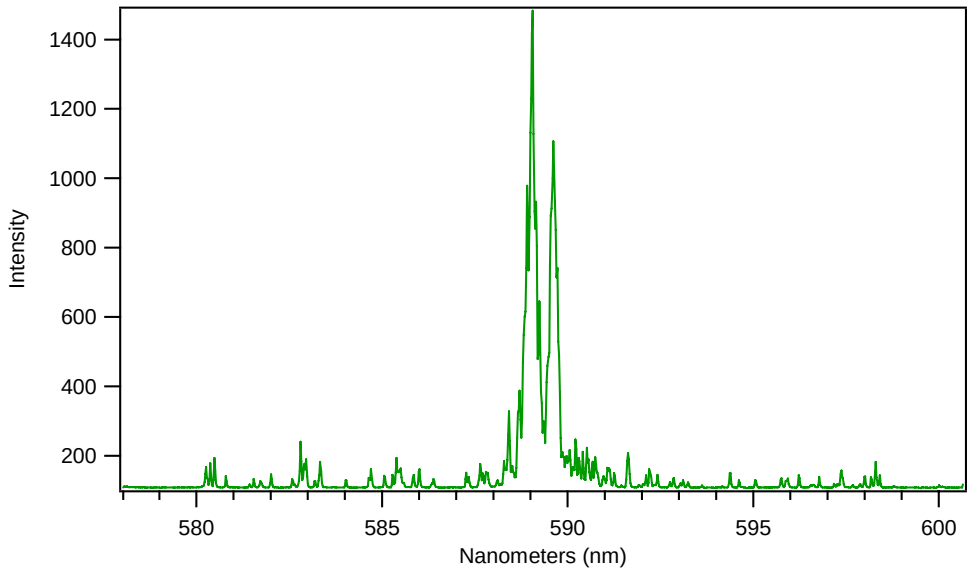

Figure 7. Spectrum of sodium D-lines at 588 and 589 nm collected on Princeton Instruments spectrometer system.

Discussion

Figure 8 describes melt activity for a set temperature over time for three generic temperatures that lead to over melting, acceptable melting and under melting. Early processes include water evaporation, decomposition and sublimation. As the melt progresses further processes such as volatilization, fining and glass formation occur. The key to a successful melt is to supply the right amount of energy at to not over melt or under melt. Over melting can produce wasted energy and potential loss of key chemical reaction due to volatility. Under melting will waste energy due to prolonged melt times or lack of glass formation.

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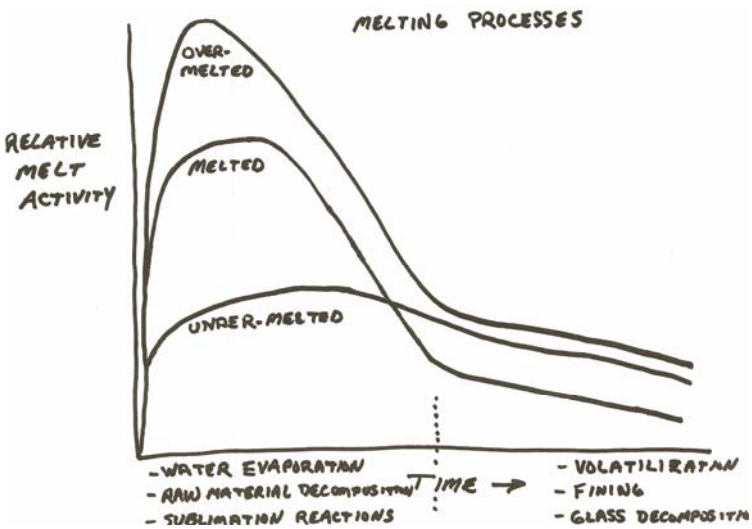

Figure 9. Overview of melt activity as a function of time at three different temperatures (with permission, Amundson [11]).

The process of glass melting involves chemical and physical changes as the "batch" transitions from individual components to a collection of bridged and non-bridged bonds. Enough energy must be supplied to the system to effectively allow bonds to break. This is not a homogeneous process since each component has its own melting point.

Table 2 shows the melting and boiling points (decomposition) of each component used in the batch used for this work (reference CRC)

Table 2. Batch components melting point/decomposition and boiling point temperatures

Component	Melting point(ºC)	Boiling Point/Decomposition (ºC)
Sand	1700	2230
Alumina(hydrated)	2000	2980
Sodium Carbonate	850	850 decomp.
Litharge	888	1470
Barium Carbonate	1300	1300 decomp.

The carbonate species will decompose into their oxides and carbon dioxide. Sodium oxide and barium oxide have boiling points of 1275 ºC (sublimes) and 1923 ºC respectively. As decomposition progresses the caustic oxides, as well as lead oxide, will react with the refractory components to form new bonds. This will establish the glass network.

As temperatures continue to climb, sublimation and evaporation will eventually establish equilibrium of gas phase components above the melt that should follow the general curve structure shown in figure X as a function of time. The appearance of each component will depend on their respective boiling point. The oxides of sodium, barium and lead have the lowest boiling points in this system and are closest in temperature to that of our heat source. Figure X shows signals obtained at 1, 3 and 5 mm above the melt surface in a platinum boat. The downward trend of signal as a function of distance follows from the gases encounter with cooler atmospheric gases to produce condensation.

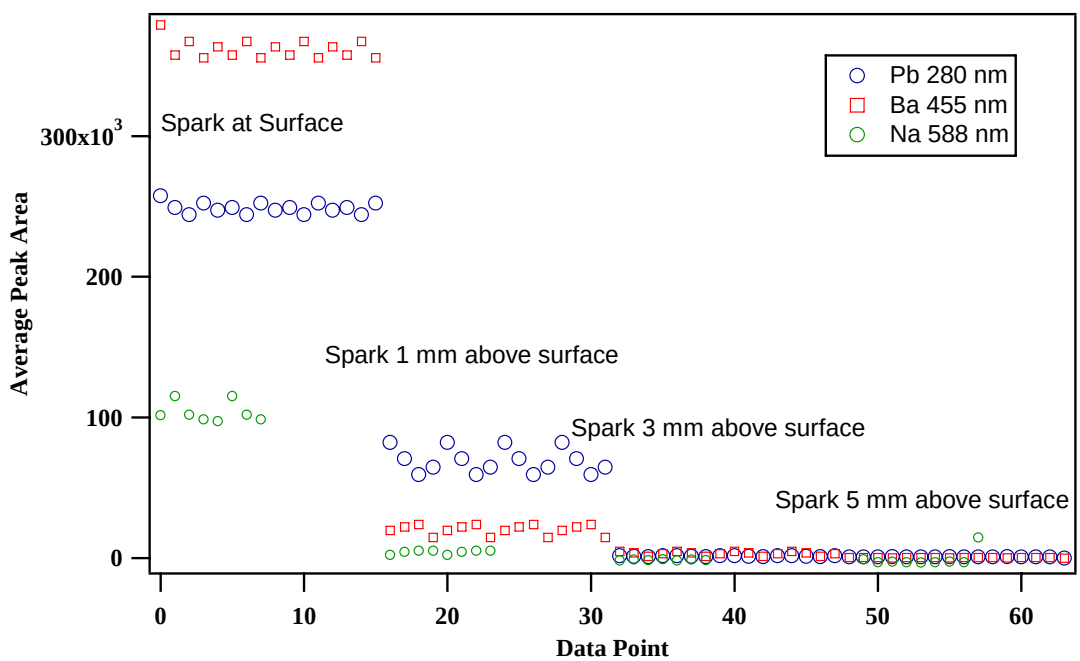

Figure 9. Signal peak area as a function of distance from the surface of the glass melt.

. The relative signal intensities are a function of batch composition, boiling point as well as signal intensity for the emission line chosen for the experiment. Though lead is highest in composition of the batch materials it shows a lower signal than barium or sodium. At the melt surface the greatest intensity comes from barium followed by lead and then sodium. The relative intensity does not stay the same going from the melt surface to 1 mm above the melt. At 1 mm above the melt the lead intensity becomes greatest followed by barium and then sodium. This does not follow what is expected based on the relative order of their boiling points (Na<Pb<Ba). This could indicate some type of gas phase species that differs in volatility from oxides that are assumed to be present. At 3 mm above the melt the intensity order is dominated by barium followed closely by sodium then lead. At 5 mm above the melt all signals are about the same and raw spectra indicate that the signals are very near background noise levels.

Conclusion and Future Work

This data shows that even in a lab scale experiment LIBS can successfully record the presence of gas phase elements species above a glass melt. We have not produced data that can be used to interpret the gas phase environment of a melting tank near the melt surface. We found it difficult to track the near surface gas phase contents through the entire course of melting as sonic perturbation causes batch materials to dominate the near surface region. In a continuous melting operation there will always be a "scum" of dissolving batch material at the surface of the melt. This could complicate measurements but remember the temperature drop going away from the near surface is lower in a production furnace than our setup in ambient air. The experiment in a production furnace should allow for higher gas phase concentrations further from the batch surface and reduce the chance of sonic perturbations of batch dust.

The major problem to overcome is that of forming a plasma inside a tank and then getting emission signal out again. Others have built systems the can withstand the hot tank environment but their arrangement requires cooling to allow the lens or fiber optic to survive [11,12]. This cooling could affect the element ratios being probed in the near surface measurement. A LIBS instrument with long focal length for plasma formation could be a solution but a long focal length for the collection optics would drastically reduce the signal and for most melting tanks this is not reasonable.

One possibility is to use the concept of collecting the gasses at the near surface and analyzing them remotely. Tong et al have done this by collecting the gasses in an acid/aqueous trap to be later analyzed by ICP emission. These gases could easily be pumped to form an aerosol stream of condensed matter that can be analyzed by the LIBS instrument outside of the hot tank. A platinum tube, as used by Tong, would be resistant to most any glass composition and the harsh environment that accompanies melting glass. It also has high thermal conductivity so it would come to temperature quickly and not condense gases at the near surface.

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