ANALYZING GLASS WITH LASER INDUCED BREAKDOWN SPECTROSCOPY

APPLICATION NOTE LIBS-027 (A4)

Introduction

The specific elemental composition of industrial glass products influences several of its physical properties, such as heat and shock resistance, transparency, and chemical reactivity. Chemical analysis of glass samples is therefore required to support both R&D and production operations. Unfortunately, full elemental analysis of glass by a method like ICP-OES requires digestion with hazardous acids and use of fusion apparatus. Adding to the challenge, some of the elements of most interest can be difficult to detect with typical techniques (such as B, Li), or preparation reagents may contaminate instrumentation causing high background or corrosion.

Laser Induced Breakdown Spectroscopy (LIBS) offers an alternative to other techniques for glass analysis. LIBS is a reagent free, direct sampling method, where the high energy laser pulse focused to the sample surface serves to both ablate a small amount of material directly from the sample and generate atomic emission from the ablated particles. LIBS is also quite sensitive to low atomic number elements like B and Li, and can measure virtually any other element important to the glass manufacturing including the primary Si oxide ingredient, to mid and low concentration elements like Mg, Al, Ca, Sr, O, Na, K, and Ba. This full-element capability may be used qualitatively to match unknown glass samples to their source, and has shown promise in forensic investigations.

This note reports results of qualitative and quantitative analysis of two glass types—a borosilicate glass used in electronic displays and commodity soda-lime glass like used in food containers.

Results

A ChemReveal® Desktop LIBS analyzer equipped with a 50 mJ, 266 nm pulse laser and a proprietary emission spectrometer was used for direct analysis of glass pieces. The choice of the 266 nm laser is important in order to achieve an efficient and repeatable ablation form the glass surface. Most common glasses, including our samples, are transparent in visible and near-infrared wavelengths whereas our ultraviolet laser wavelength is absorbed, resulting in a shallow and well-focused depth of analysis. The samples were analyzed under an Argon purge in order to enhance the sensitivity for elements present at lower concentrations.

Boron in Borosilicate Glass

Figure 1 shows a typical LIBS spectrum of a glass from an electronic display. The high spectral resolution of the ChemReveal spectrometer allows separation and identification of the many elements in the sample over a wide range of concentrations. In the first set of samples, the boron concentration was the most important element influencing the performance of the product. Figure 2 expands the spectral range to show the region useful for quantification of boron. The spectra are normalized to the intensity of the silicon emission line to make the boron intensity comparable between samples. It is obvious the boron concentration of these six samples varies substantially, from low concentration of sample 1, to much higher concentration in samples 3 and 5. In order to quantify the differences, a calibration curve was developed from similar glass standards with known boron concentration. The results of the calibration and the predicted concentrations of the unknown glass samples are shown in Figure 4. We see the boron concentration ranges from 0.3% to as high as 11%.

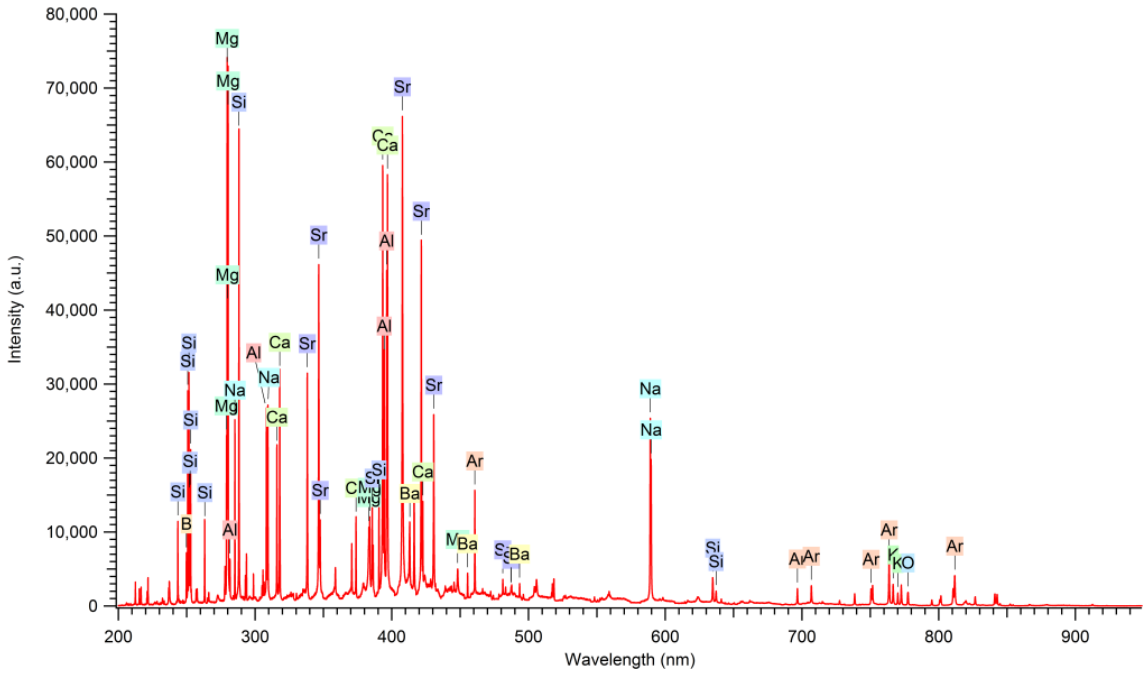

Figure 1: Typical LIBS spectrum of a glass sample over the full spectral range

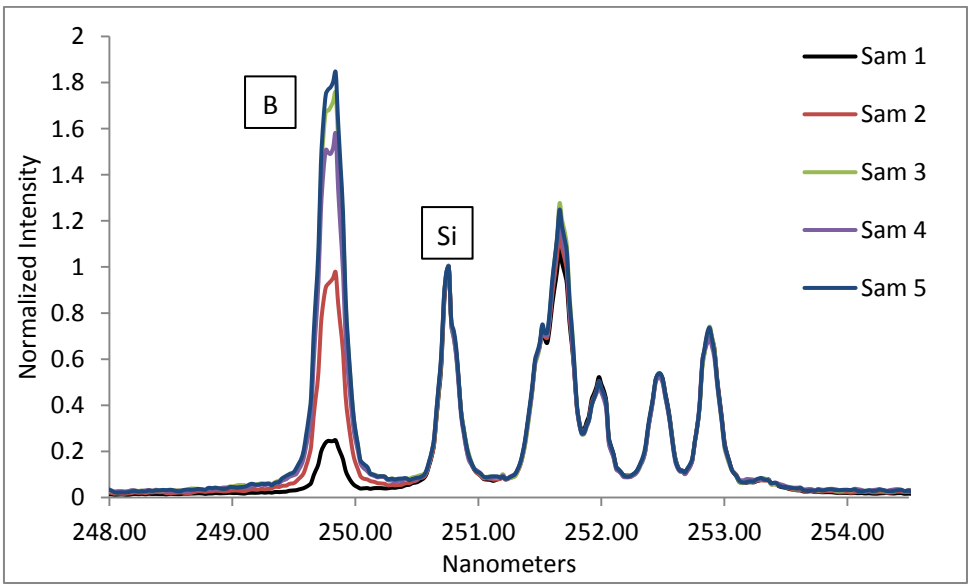

Figure 2: LIBS spectra of the of glass samples focusing on the Boron peak. Each spectrum is average of 25 ~50 mJ laser shots. The spectra are normalized to the bulk silicon peak to show the variation in Boron intensity which is proportional to concentration.

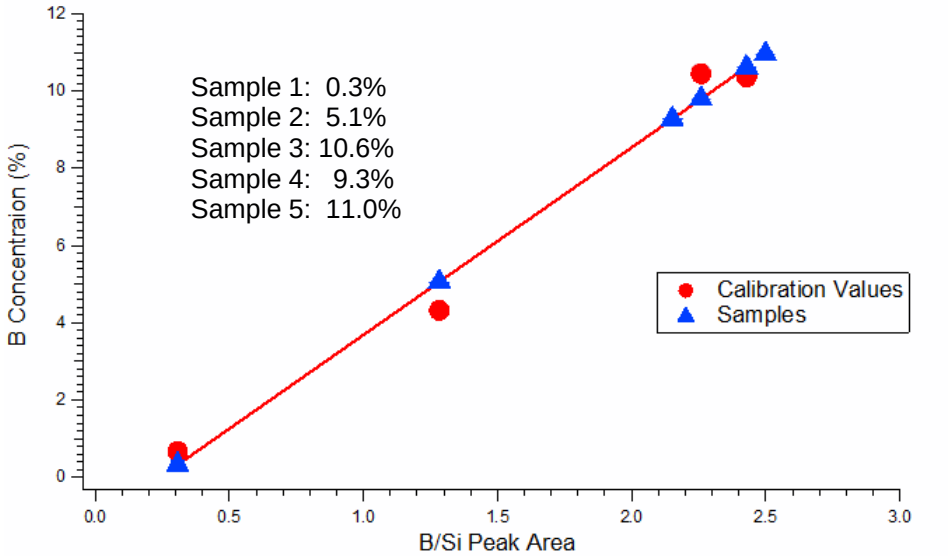

Figure 3. Determination of boron concentration in borosilicate glass samples using a 4 point calibration.

Major and Minor Elements in Soda-Lime Glass

In a second study, three standard reference materials, SRM 620, 621 and 1830, were analyzed by both ICP-OES and LIBS in our laboratory to compare the results. For ICP analysis, the glass samples were ground, weighed, digested over a period of hours, with HNO3/HCL/HF acids and then finally diluted to appropriate concentration. The ICP analysis allowed measurement of elements not included in the certified analysis report, such as lithium. The ICP results are shown in Table I. Note the good agreement of the major elements, Na, Ca, and Mg (reported as oxide), gives us confidence the non-certified value for lithium is accurate.

		Na_2O	CaO	MgO	Li_2O
SRM 620	**Calculated**	14.56	7.09	3.79	0.0119
	Expected	14.39	7.11	3.69	
	Recovery	101.2%	99.7%	102.7%	
SRM 621	**Calculated**	12.77	10.68	0.27	0.0241
	Expected	12.74	10.71	0.27	
	Recovery	100.2%	99.7%	100.0%	
SRM 1830	**Calculated**	13.73	8.41	3.92	0.0067
	Expected	13.75	8.56	3.90	
	Recovery	99.9%	98.2%	100.5%	

Table I: Calculated concentrations and recoveries for selected oxides in soda-lime glasses as determined by ICP-OES analysis. Al concentrations in % by mass.

For the LIBS analysis, the SRM glass pieces were analyzed directly without any sample preparation. To improve precision, ten laser shots were collected at each point of 9 3x3 grids for a total of 810 laser shots (about eight minutes total collection time, with no sample preparation time). Figure 4 shows the calibration curves developed from these data. These curves were then used to predict the concentrations of a fourth standard reference material, SRM 1831, as shown in Table II. The recovery—the agreement to certified values—is comparable to our ICP analysis for the major elements. Note these LIBS results also give us the concentration of Li in the sample at much lower concentration within the same analytical run. The recovery for lithium is calculated using results from an ICP analysis following the same protocol used on the calibration samples.

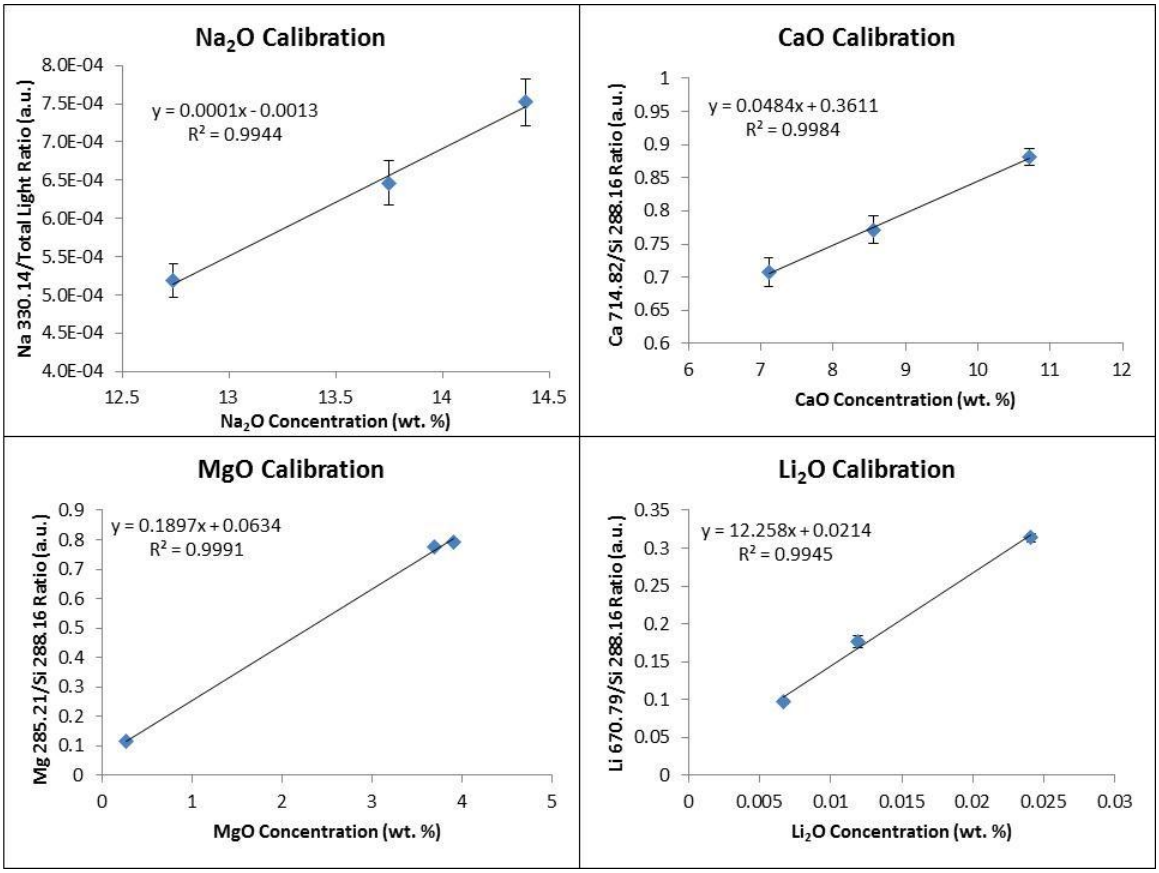

Figure 4. LIBS calibration curves using known concentrations from the ICP-OES data. The emission lines selected where 330.1 for Na, 714.8 for Ca, 285.2 for Mg, and 670.8 for Li, each ratioed to an appropriate reference.

	Na_2O	CaO	MgO	Li_2O
Calculated	13.78 ± 0.54	8.23 ± 0.25	3.58 ± 0.02	0.0174 ± 0.001
Expected	13.32	8.20	3.51	0.0165
Recovery	103.5%	100.4%	102.0%	105.4%

Table II: Predicted concentrations and recoveries for selected oxides in soda-lime glasses as determined LIBS Analysis. All concentrations in % by mass. Expected concentrations of Na, Ca, and Mg are the certified values. Expected concentration from Li is from ICP analysis of the sample.

Summary

The ChemReveal LIBS Desktop Analyzer is a rapid method for analyzing glass samples. Glass can be analyzed directly with no sample preparation. LIBS is also quite sensitive to low atomic number as we have shown for Boron and Lithium, elements that can be important in influencing the properties of glass, or for identifying the source of the sample material. In order to develop LIBS calibrations, matrix matched standards of known concentration are required. As shown here, the accurate but time consuming ICP-OES analysis is very valuable tool for characterizing standard samples for use in LIBS calibrations. In this way, ICP and LIBS support each other in the analytical laboratory.

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