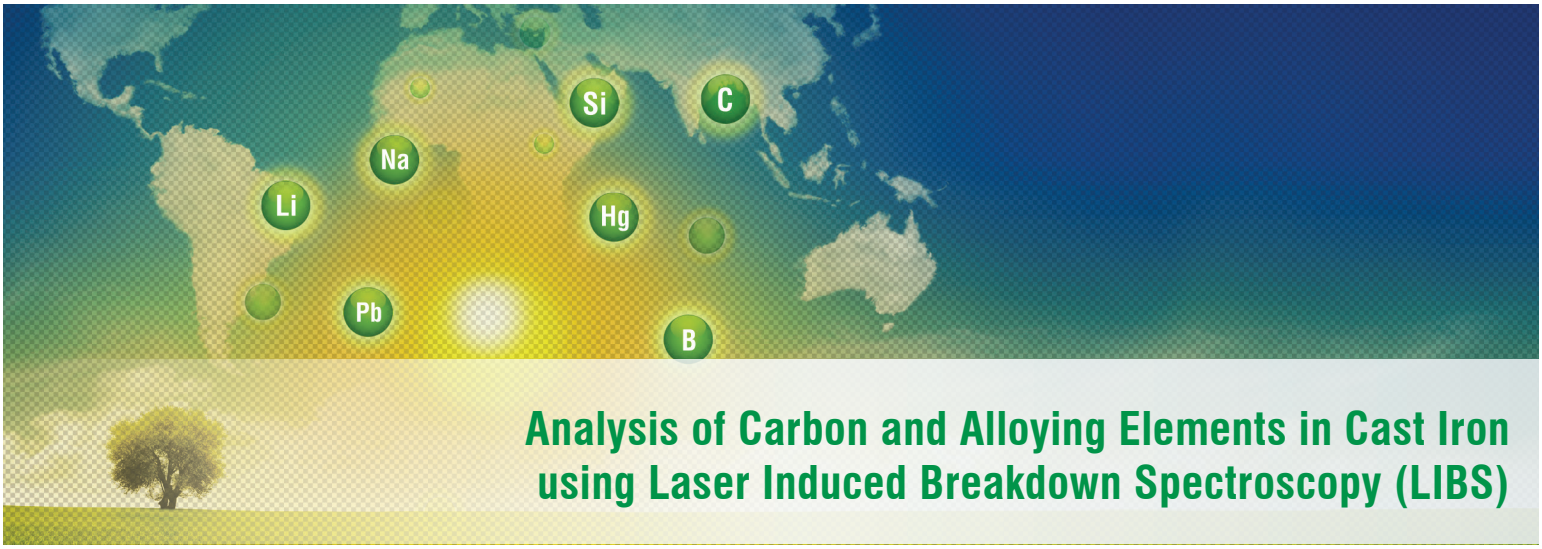


Analysis of Carbon and Alloying Elements in Cast Iron using Laser Induced Breakdown Spectroscopy (LIBS)

In today's iron foundries, the labs are faced with a large volume of daily samples comprised of raw materials, base iron, post treatment iron, and actual castings. There are various types of cast irons with different target physical properties such as tensile & compressive strength, hardness, machinability, and corrosion resistance. The production of different cast irons depends on the nature of heat treatment processes and the composition of carbon and other alloying elements such as Cr, Mo, Cu, and Ni.

Cast iron and As-Cast analysis have proven to be challenging to produce accurate and reproducible results. For example, carbon which is typically present from 2 to 4% in cast irons is present in various forms that range from tiny graphite spheroids (nodular cast iron) to large flakes (gray iron). The popular Spark/Arc OES technique requires a pre-burn time for surface homogenization, but some of free carbon preferentially evaporates during pre-spark and inaccuracy in quantitative result arises. For GDS (Glow Discharge Spectrometry), a long pre-burn time is necessary to obtain stable signals of carbon and other elements in the ferrous material.

The J200 LIBS (Laser Induced Breakdown Spectroscopy) Instrument from Applied Spectra provides an alternate approach for performing quantitative analysis of carbon and other elements in all cast irons. The J200 LIBS uses short laser pulses to deliver high power density into the sample surface and directly excite tough materials like carbon flakes for rapid OES analysis. The effective excitation of all phases of materials in the cast irons allows the J200 LIBS Instrument to perform accurate and rapid quantitative analysis of carbon and other important elements for the cast iron samples without necessity for a long pre-burn.

The J200 LIBS Instrument also analyzes all other elements in the periodic table from Hydrogen to Plutonium, including lighter elements and non-metals such as Li, B, H, N, O, S, and F. The measurements can be performed in air or using low flow of Argon purge gas (mls/min versus liters/min), significantly reducing the cost of operation (COO). The J200 LIBS provides high versatility in performing spatially resolved analysis with a laser spot size as small as 10 micron for 2D and 3D mapping analysis. Finally, the J200 LIBS is an excellent QC tool with the capability to classify metal and metal alloy samples based on fingerprint-like LIBS spectra associated with specific metal products.

In this current study, the J200 LIBS Instrument was used to demonstrate the quantitative analysis of carbon and other alloying elements in cast iron samples. A powerful LIBS capability to perform 3D elemental imaging and classify different type of cast irons was also demonstrated.

Operating Parameters

Applied Spectra's J200 LIBS Instrument

- 266 nm Nd:YAG laser
- Broadband CCD ES detector
- Applied Spectra Axiom Operating System Software
- Flex™ LIBS sample chamber
- Air environment
- 9 Brammer cast iron standards
- Clarity LIBS software for quantitative analysis, 3D elemental mapping, and PCA analysis.

Applied Spectra's J200 LIBS Instrument (ES model)

Quantitative Analysis

Table 1 summarizes the Brammer standards used for the analysis of carbon and 4 other alloying elements (C, Cr, Mo, Cu, and Mn). These standards cover carbon concentration range from 2.4% to 4.5%. Five of these standards are gray irons while two represent the cast irons with Mg.

Concentrations (wt.%)						
		C	Cr	Mo	Cu	Mn
BS 20E	Gray iron	3.24	0.088	0.042	0.23	0.8
BS 20G	Gray iron	3.33	0.086	0.19	0.54	0.58
BS 20P	Gray iron	3.22	0.079	0.033	0.067	0.63
BS 20R	Gray iron	3.25	0.094	0.053	0.35	0.62
BS 20W	Gray iron	3.27	0.092	0.054	0.29	0.62
CZ SPL17 35A	Cast iron C>2.75%	4.55	0.022	0.003	0.004	0.096
CZ 20034 11b	Cast Iron C<2.75%	2.44	1.178	1.144	0.13	0.382
CZ SPL17 34A	Cast iron with Mg	3.48	0.102	0.072	0.23	0.98
CZ SPL17 42A	Cast iron with Mg	3.94	0.145	0.021	0.199	0.764

Table 1 Certified concentration of elements for Brammer standards (cast iron)

LIBS emission spectra (190 to 1040 nm) was collected using the J200 LIBS Instrument. A laser beam at a spot size of 200 micron was rastered in a line pattern. Figure 1 shows an example of entire BS W20 LIBS spectrum resulting from this line raster together with several zoom-in spectral regions for C, Cr, Mo, Cu, and Mn. As seen from the figure, LIBS is effective in detection of all target elements including carbon.

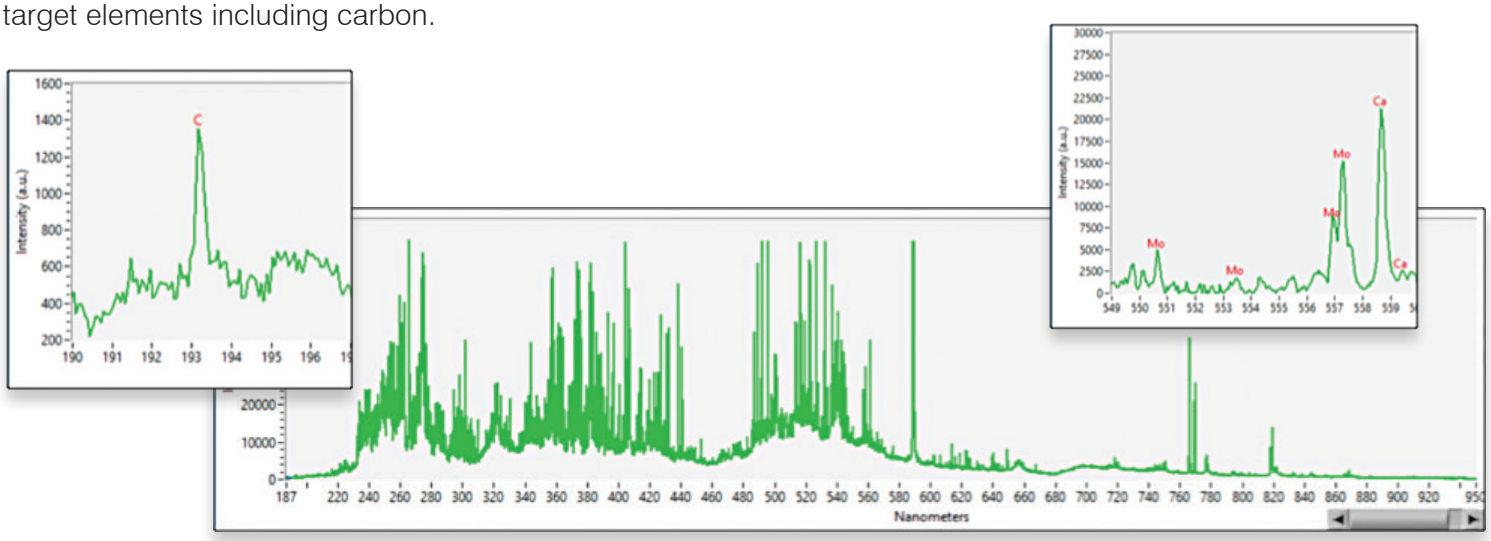
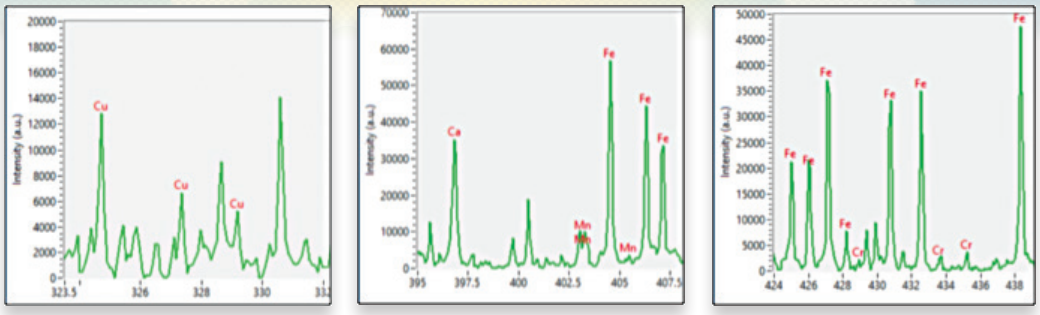


Figure 1 Example LIBS spectrum for sample BS 20W (grey iron) (C at 3.27% wt., Cr at 0.092% wt., Mo at 0.054% wt., Cu at 0.29% wt., and Mn at 0.62% wt.)



Using Clarity LIBS data analysis software, an advanced multivariate calibration model was generated. This model uses 10 broadband LIBS spectra resulting from 10 laser raster lines for 8 Brammer standards excluding BS 20W to form a spectral library. The figure 2 shows the calibration curves obtained for C,Cr, Mo, Cu, and Mn.

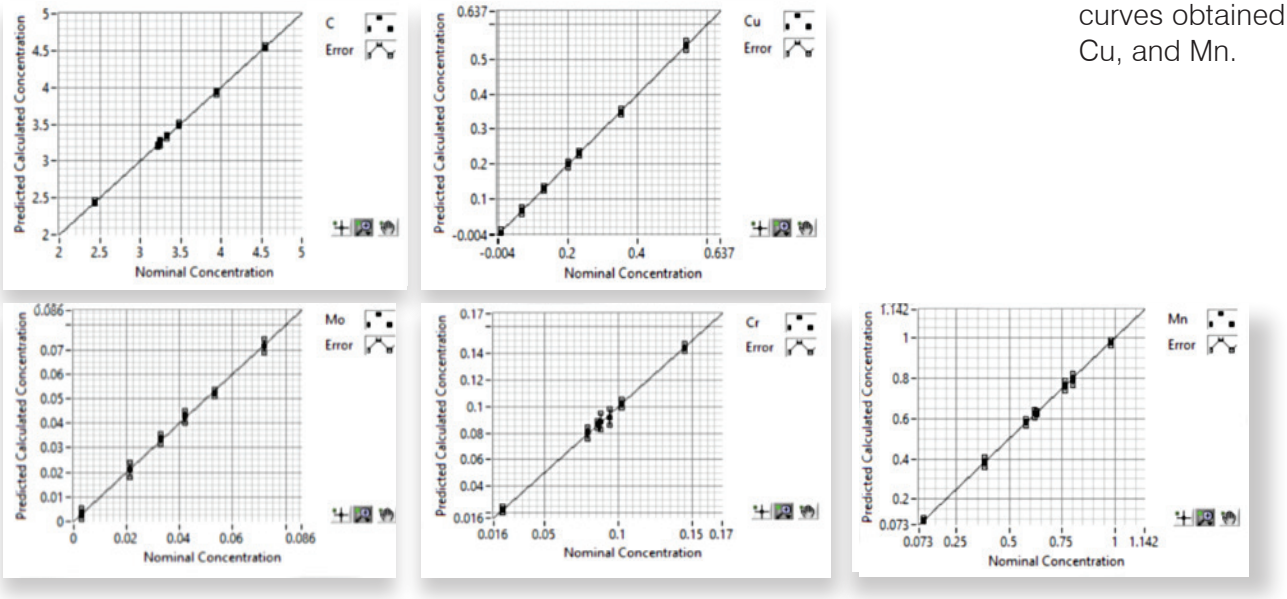


Figure 2 Multivariate calibration curve generated by the Clarity LIBS software for C, Cr, Mo, Cu, and Mn

Table 2 displays the result for bias performance when BS 20W gray iron was used as an unknown to test the calibration model. The accuracy of the method was good with bias performance ranging from -7 to 6% across different elements.

Concentration Results for BS 20W (wt.%)					
	C	Cr	Mo	Cu	Mn
Estimated Concentration	3.08	0.09	0.05	0.28	0.66
certified value	3.27	0.092	0.054	0.29	0.62
% Bias	-6	-2	-7	-3	6

Table 2 Accuracy of the multivariate calibration method for test using BS 20W standard as unknown

3D Carbon Distribution Imaging and Cast Iron Classification by LIBS

The BS 20W gray iron was ablated in a 10 X 10 grid pattern over 3.5 mm X 3.5 mm area. At each of the grid point, 25 laser pulses were applied using a 200 micron spot size (Figure 3). The carbon intensity line at 193 nm was background-subtracted for all LIBS data collected over all analyzed points. Using Clarity LIBS software, 3D carbon concentration map was generated by converting integrated carbon line intensity into local concentration value using a simple univariate calibration curve. For this mapping analysis, 7 Brammer standards (CZ 20034 11b, CZ SPL17 35A, CZ SPL17 34A, CZ SPL17 42A, BS 20E, BS 20P, and BS 20R) were used to correlate average integrated carbon line intensity to concentration (wt.%) (Figure 4). As seen from Figure 5, the J200 LIBS Instrument provides the powerful way to visualize the carbon distribution in cast irons. The same distribution analysis can be performed for any alloying or trace elements for homogeneity check or local maldistribution analysis.

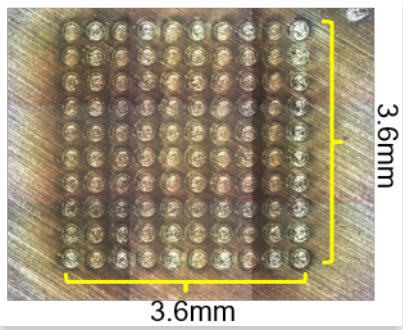


Figure 3 10 X 10 grid for 3D imaging of carbon over 3.5 mm X 3.5 mm area

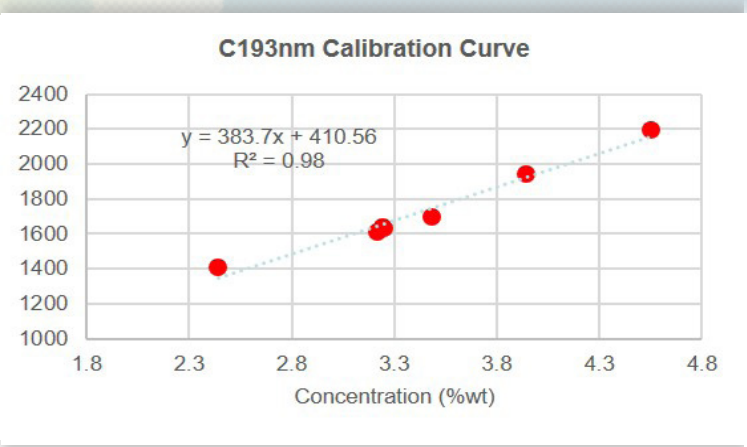


Figure 4 Univariate Carbon calibration curve for 3D Carbon mapping analysis

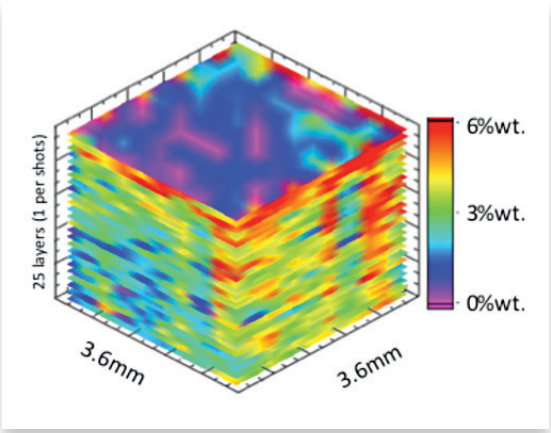


Figure 5 3D elemental map of carbon in gray iron BS 20W

LIBS data is effective in classifying different cast irons. Figure 6 shows the Principle Component Analysis (PCA) result based on LIBS spectra collected for all 9 Brammer standards. There are 4 main groups of clusters in the PCA plot. These groups were mainly gray iron, cast iron with Mg, cast iron with >2.5% carbon and cast iron with <2.5% carbon. The gray iron standards had similar Mn and C concentration from one another and closely clustered together in the PCA plot. The cast irons with Mg also clustered separately from the rest of the standards due to Mg content in these standards. The PCA based on LIBS spectra thus can be an excellent approach for classifying cast irons or checking non-conforming products in terms of its chemistry.

Conclusion

The J200 LIBS Instrument is a powerful and versatile elemental analyzer for cast iron applications. It can perform a rapid quantitative analysis of carbon and other alloying elements without for pre-burn requirement for more accurate analysis. The instrument can also provide depth profiling and 3D mapping of critical elements, all included with no additional hardware. Powerful, yet easy to use Clarity LIBS data analysis software makes the visualization of the mapping results effortless. With low cost of operation due to no or minimal argon consumption, LIBS is ideal for rapid QC for raw materials in production and the analysis of As-Cast to confirm the elemental composition of the finished castings.

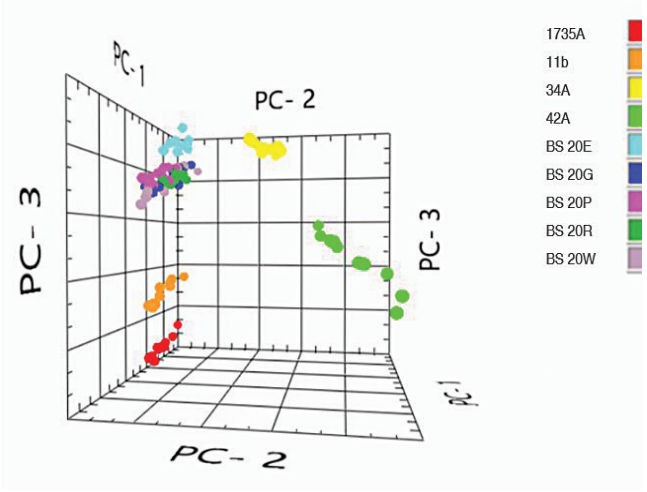


Figure 6 PCA Classification of cast iron standard

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