

# Automated Chemical Analysis of Liquid Aluminum for Process Control

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## Abstract

We report on automated analysis of the trace element content of liquid metal, implemented in a casthouse of a primary aluminum smelter. The automated analysis involves robotic sampling from transport crucibles followed by a direct measurement of the chemical content of the liquid metal using laser-induced breakdown spectroscopy (LIBS). Experiments were carried out on-site over a period of several months, sampling over 200 crucibles and comparing the LIBS analysis with conventional laboratory spark-OES analysis of solid samples collected from the same crucibles. We discuss the predictive power of LIBS analysis for different elements, confirming that automated analysis of the molten metal can replace manual laboratory analysis for process control for many common trace elements.

Keywords: LIBS, aluminum, process technology, chemical analysis

## Introduction

In recent years, laser-induced breakdown spectroscopy (LIBS) has emerged as a promising technology for online chemical analysis, including direct analysis of molten aluminum [1-3], although reports of actual industrial implementations are still somewhat limited [4]. Previously, we have reported the application of LIBS analyzers to trace element analysis in liquid aluminum down to ppm concentrations [5], also confirming its repeatability and stability for several important trace and alloying elements [6]. In the present paper, we report on the application of a fully automated LIBS analyzer to casthouse process control, where crucibles are analyzed prior to furnace loading. In order to provide benchmarking for the liquid metal analysis, results from online analysis are compared to laboratory measurements of solid samples collected from the same crucibles.

## Casthouse implementation

An industrial LIBS analyzer with robotic sample handling (EA-2500, DT-Equipment) was positioned at a crucible skimming station (Fig. 1a) in the casthouse of Century Aluminum's Nordural primary aluminum smelter (Grundartangi, Iceland). The skimming robot also serves as a sample extraction robot, collecting two samples (approximately 300 g each) from each crucible after skimming (Fig. 1b). The robot pours the first sample of liquid metal to a standard sample mold. This sample is subsequently cooled and transported to the laboratory where it is milled and analyzed by spark-OES according to standard protocols, with measurements repeated three times per sample. The second sample of liquid metal is delivered to the sample handling robot of the EA-2500 analyzer (Fig. 1c) where its sample temperature is regulated (Fig. 1d), before carrying out the LIBS analysis (Fig. 1e). Three individual measurements are performed for each melt sample. After analysis, the liquid metal is returned to the skimming ladle (Fig. 1f), from where it combines

with the aluminum in the next crucible to arrive to the skimming station, thus avoiding any buildup of the analyzed metal. The typical overall cycle time (from the time when the sample is extracted to when it is discarded) is 2-3 minutes, depending on the crucible temperature, with the time required for the actual LIBS measurement being <45 seconds. Further details of the LIBS analysis have been published previously [5,6].

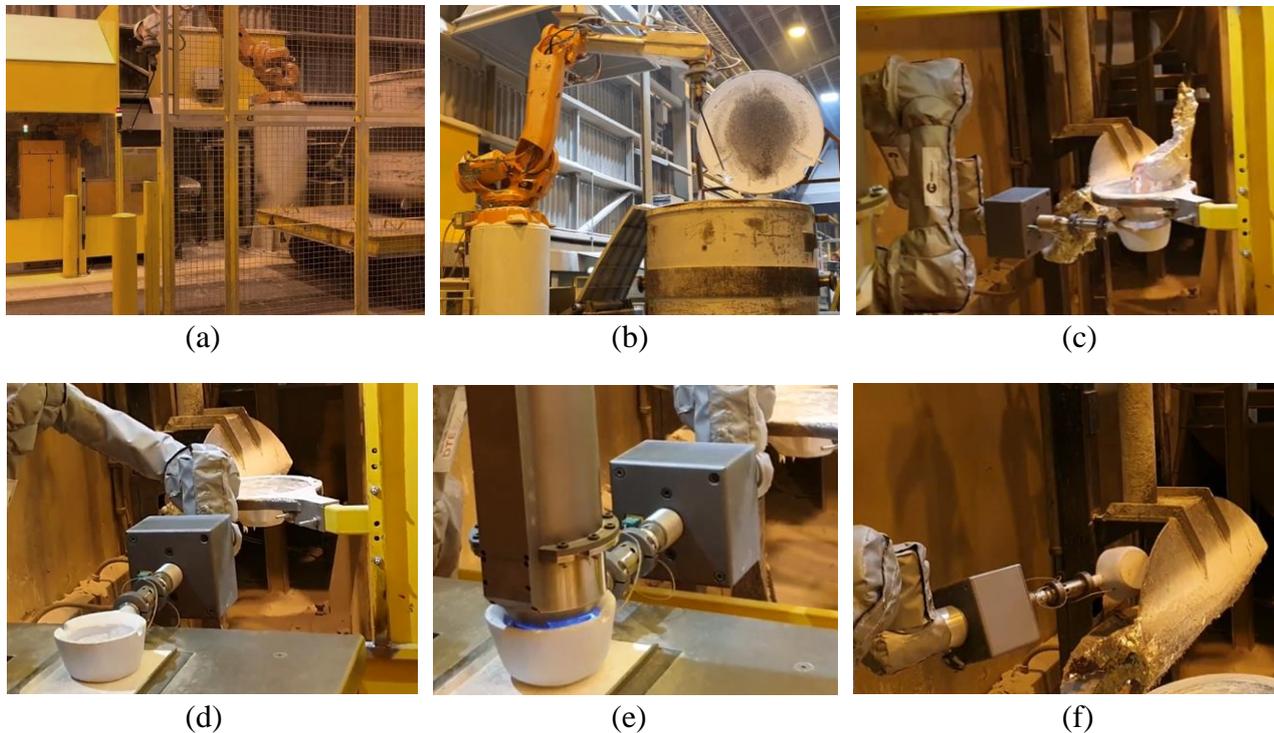


Figure 1. Steps for LIBS analysis of liquid aluminum at the crucible skimming station (a), including sample extraction (b), transfer to sample handling robot (c), temperature regulation (d), plasma excitation (e) and returning the analyzed aluminum to the skimming ladle (f).

Presented here is analysis from 223 crucibles, collected over a period of 30 days, averaging about 14 crucibles per day on the days where the equipment was running. This represents a sampling from a total of approximately 1200 metric tons of primary aluminum (during this testing phase, the analyzer was run intermittently, sampling about 5% of the smelter's overall monthly production).

## Results

In the present work, the primary focus was on monitoring the concentration of Fe and Si in the as-produced aluminum, but other minor elements were also included in the analysis, as discussed below. A comparison between the online analysis and laboratory results is shown for Fe and Si in Fig. 2. In the majority of crucibles, the measured impurity content was in the range 500-1300 ppm for Fe and 250-500 ppm for Si. Approximate concentration ranges for the other investigated impurity elements are listed in Table I.

The correlation coefficients (Pearson R) between LIBS and OES measurements for the full set of 223 crucibles were  $R=0.986$  for Fe and  $R=0.898$  for Si. It should be pointed out that a stronger correlation for these elements ( $R>0.999$  and  $R>0.9975$ , respectively) has been observed in a similar experiment when reference samples are cast *from the exact same melt* as the LIBS measurement is performed on [7]. Although the analysis is not directly comparable because of the significantly different size of the data sets, this suggests that some variance may be attributed to actual differences in the solidified crucible samples and the melt samples in the present work, rather than OES and LIBS measurement uncertainty alone.

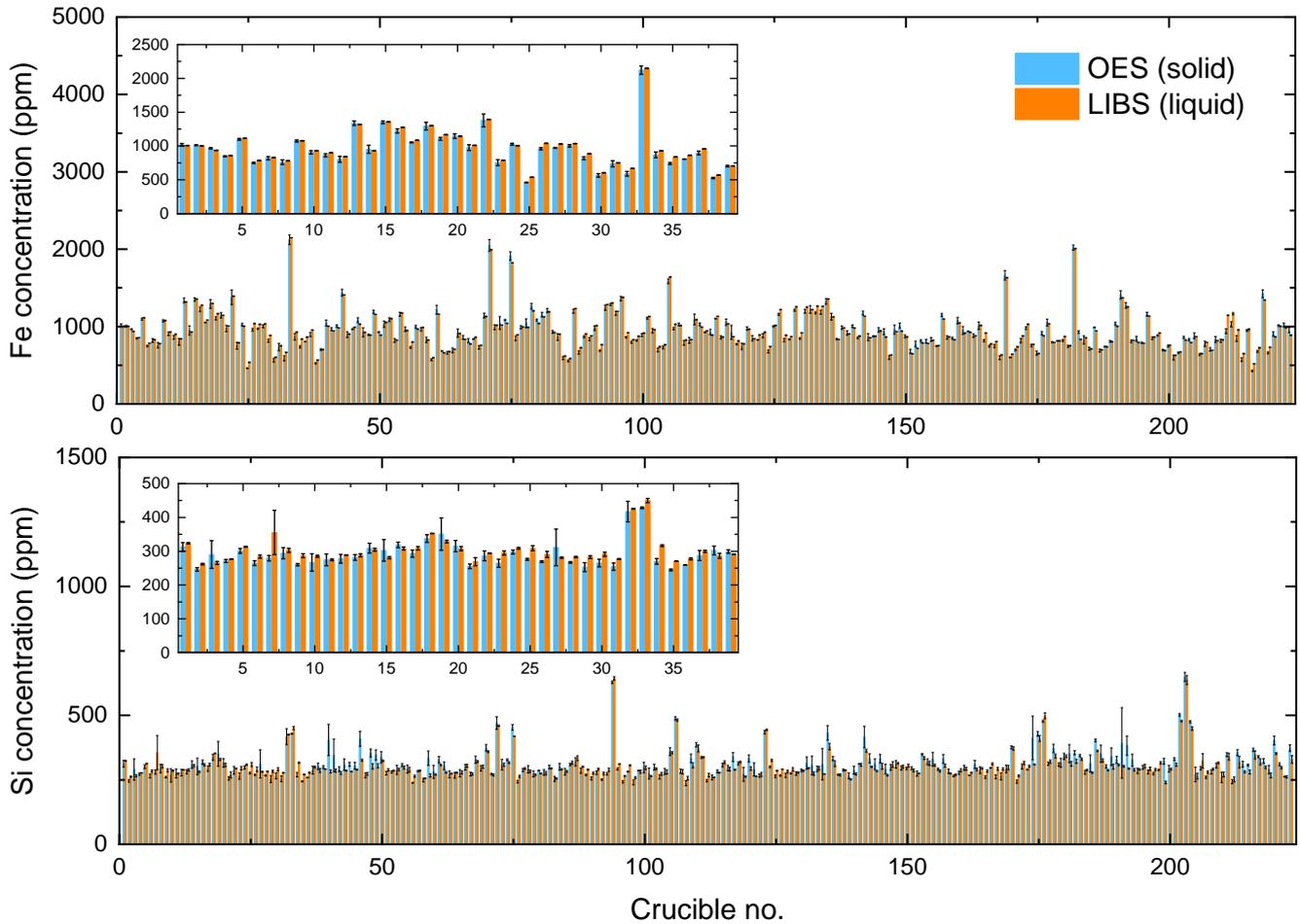


Figure 2. Comparative data for Fe and Si content of aluminum sampled from 230 crucibles. Insets show the analysis for 40 crucibles, for clarity.

Using the repeated measurements performed on each solid sample and each melt sample, sample standard deviations were determined, according to  $s = [\sum_i (c_i - c_{av})^2 / (n-1)]^{1/2}$ , where  $c_i$  is the measured concentration according to each individual measurement ( $i=1..n$ ) and  $c_{av}$  is the average of the measurements ( $n=3$ ). The relative standard deviation  $\%RSD = s/c_{av}$  of each set of three measurements was calculated and the  $\%RSD$  values were subsequently averaged over the full set of 223 crucibles. For both Fe and Si, the averaged  $\%RSD$  was approximately two times higher in OES measurements than in the LIBS measurements, in line with previous reports [6]. The observed uncertainty in the OES measurement is larger than that observed on homogenized reference standards and can, to a large degree, be attributed to the sample preparation process, rather than the OES measurement itself [8]. For the other investigated elements (Ga, V, Zn, Ni, Ti, Mn, Cu), present in much smaller concentrations, the  $\%RSD$  in LIBS measurements was similar to or larger than the  $\%RSD$  values of the corresponding OES measurements (cf. Table I).

The most important metric for gauging the quality of the online analysis is its predictive power, which depends both on the accuracy of the analyzer calibration function and the standard error of each individual LIBS measurement. In the absence of a systematic bias or drift, the standard error can be lowered by increasing the number of measurements, the tradeoff being increased measurement time. In the present case, the predictive power is evaluated relative to the OES reference measurements, while recognizing that the agreement between the LIBS measurements of the liquid metal and the laboratory measurements on the solid process samples is influenced by the random error in both measurements, possible inhomogeneity in

the solid samples and possible differences between the two samples of metal collected from each crucible. The measured difference  $\Delta = c_{av,OES} - c_{av,LIBS}$  was calculated for all crucibles and the distribution of values of  $\Delta$  for Fe and Si is shown in Fig. 3.

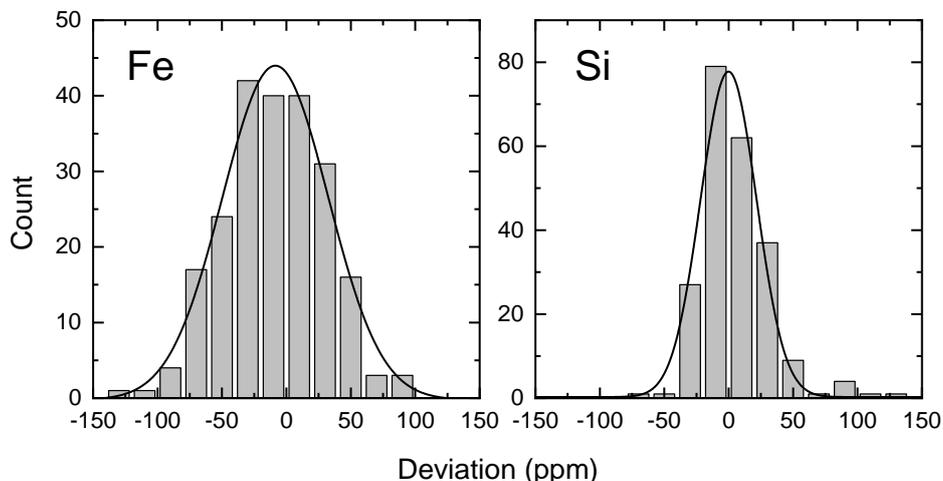


Figure 3. Distribution of differences between LIBS measurements on liquid metal and laboratory reference measurements for Fe (columns, left panel) and Si (columns, right panel). Solid lines represent normal distribution curves fitted to the data.

Gaussian curves fitted to the distributions in Fig. 3 confirm that the differences between LIBS and OES measurement results are normally distributed. The standard deviations of the data sets are  $\sigma_{\Delta} = 41$  ppm for Fe and  $\sigma_{\Delta} = 26$  ppm for Si. In other words, the results of the online LIBS analysis on the liquid metal agrees in 95% of cases ( $\pm 2\sigma_{\Delta}$ ) to within  $\pm 82$  ppm for Fe and  $\pm 52$  ppm for Si with the averaged laboratory OES result. A corresponding analysis was carried out for the other investigated elements, see Table I for a summary of results.

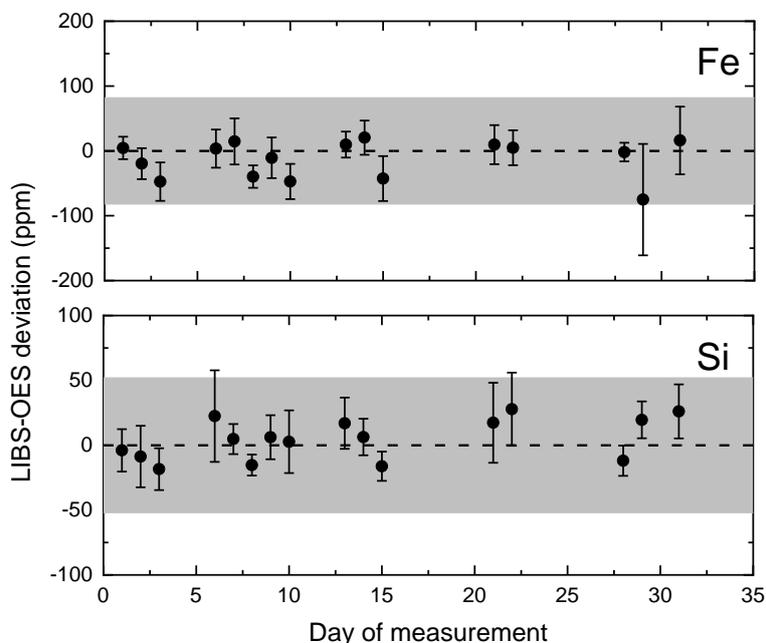


Figure 4. Day-to-day difference (average, symbols) and its distribution ( $\sigma_{\Delta,daily}$  error bars) between online measurement results and laboratory reference values, confirming the absence of significant instrument drift over the measurement period. The gray areas indicate the respective  $2\sigma_{\Delta}$  limits for the full data set.

The OES spectrometer used for reference measurements in the present work was calibrated daily. Conversely, no adjustment was made to the calibration of the LIBS analyzer during the measurement period. In order to check for the presence of systematic drift in the instrument over the measurement period, the daily average of measurement difference between the LIBS analysis and the OES results, over the full 1-month measurement interval, was determined. The results (Fig. 4) indicate that the long-term instrumental drift is significantly smaller than the statistical distribution of results caused by LIBS and OES measurement uncertainty and other random errors. This agrees with the results of previous studies where the LIBS analysis was shown to exhibit both short term (hours) [6] and long term (months) [5] stability. As shown in Table I, good correspondence between online LIBS analysis and OES reference analysis is observed for elements present in concentrations as low as 5-15 ppm.

Table I. Observed instrumental uncertainty and absolute difference between LIBS analysis and OES reference measurements for the investigated elements.

Element	Conc. range (ppm)	Av. %RSD OES	Av. %RSD LIBS	LIBS-OES difference st.dev. (ppm)
Fe	500-1300	2.7%	1.6%	41
Si	250-500	4.1%	1.7%	26
Ga	60-140	2.9%	2.1%	12
V	40-100	1.9%	6.9%	6.1
Zn	20-80	2.7%	15.8%	9.9
Ni	20-60	4.0%	10.3%	6.6
Ti	20-60	1.4%	3.5%	4.1
Mn	5-20	4.6%	12%	1.8
Cu	5-15	8.6%	8.5%	1.4

It should be emphasized that for the purpose of this study the data was not filtered to remove outliers or measurement results with low internal consistency. Correlation coefficients and absolute agreement between LIBS and OES results can be further improved, for example, by rejecting measurements that show an internal %RSD above a certain value. In an industrial process control setting, time constraints may prohibit extracting a new sample for analysis, when measurement of a previous sample is judged insufficiently accurate. However, the number of measurements performed on an already collected sample can readily be increased to identify and eliminate individual outliers that may occur due to, e.g., presence of inclusions or other inconsistencies in the measurement process itself. Imposing a requirement for internal agreement (%RSD) of <5% for Fe measurements in the present data set, for example, would exclude about 8% of OES measurements and 2% of LIBS measurements. For the filtered set of Fe measurements, correlation is improved slightly (to  $R=0.989$ ) and the OES-LIBS difference distribution width ( $\sigma_{\Delta}$ ) is reduced from 41 ppm to 39 ppm. In the case of Si, a <10% internal agreement requirement on the present data set excludes about 6% of the OES measurements and 0.5% of the LIBS measurements, improving

correlation to  $R=0.93$  and reducing  $\sigma_{\Delta}$  to 22 ppm. As this example illustrates, the importance of such measures will, in general, be element-dependent and must be judged based on the level of measurement accuracy required at the particular point in the production process.

### **Conclusions**

We have shown that automated LIBS-based analysis of chemical composition of liquid primary aluminum gives a good representation of melt chemistry, typically deviating less than 10% from laboratory results and in some cases showing improved internal consistency of measurement results, compared to laboratory analysis of process samples. The online analysis provides rapid results (typically <3 minutes from time of sampling), improves worker safety and eliminates risk of human error. The LIBS analyzer can run uncalibrated for weeks or months and is ideal for continuous process control where fast and secure feedback is required.

### **Acknowledgements**

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