

# Accurate Real-Time Elemental (LIBS) Analysis of Molten Aluminum and Aluminum Alloys

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## Abstract

Real-time LIBS (laser induced breakdown spectroscopy) analysis for monitoring and process control in an aluminum smelter is reported. Chemical analysis was carried out directly in a casting launder as well as with robotic sample feeding at a crucible skimming station. Using this system, ppm-level quantification limits have been demonstrated for certain trace elements. For most of the elements studied, measurement uncertainty is lower than observed in OES (optical emission spectroscopy) analysis on corresponding process samples. Furthermore, LIBS analysis allows the time-varying concentration of elements in the melt to be monitored on a minute-by-minute basis. Our results confirm that for many technologically important elements, LIBS analysis represents a competitive alternative to laboratory OES, provided that suitable access to the liquid aluminum can be ensured. This approach improves plant safety by reducing the need for manual sampling of liquid metal, eliminates operator-related errors in chemical analysis and is critical for automation of casthouse operations.

## Keywords

LIBS • Aluminum • Chemical analysis

## Introduction

Efficient process control in aluminum smelters and casthouses relies on frequent and reliable chemical analysis of the metal or alloy. The most common approach involves manual sampling and subsequent laboratory analysis of

solidified samples using arc-spark Optical Emission Spectroscopy (spark-OES). Manual sampling, sample preparation and measurement carries the risk of introducing measurement errors including, but not limited to, segregation of elements during solidification, contamination of molds and tools, cracks or voids, incorrect milling depth or sample surface roughness outside specifications [1]. In addition, the sampling and measurement process is time-consuming and involves safety hazards related to handling of liquid metal and transportation of physical samples within the smelter or casthouse. In primary smelters, real-time measurements of electrolyte properties have in many cases already replaced off-line laboratory analysis. Technologies such as the STARprobe™ developed by Alcoa [2, 3] or the Heraeus FiberLab™ [4], while not fully automated, have greatly decreased the need for collection, transportation and centralized laboratory analysis of bath material samples.

The potential of Laser-Induced Breakdown Spectroscopy (LIBS) for direct real-time chemical analysis of molten metal has been discussed for decades and some industrial implementations have already been tested [5–10]. LIBS falls into the category of atomic-emission spectroscopies and employs a high-energy laser pulse (instead of, e.g., an electrical spark in OES) to generate a plasma that subsequently emits atomic radiation. In spite of its many obvious advantages, however, the adoption of LIBS in industry is still limited and mainly focused on metal scrap sorting and alloy identification [11]. In the present paper, we report on the use of LIBS for real-time chemical analysis of aluminum.

## Implementation

The performance of an industrial LIBS analyzer (EA-2000, DT-Equipment [12]) was evaluated at a casting launder system (Fig. 1) as well as with robotic feeding at a crucible skimming station (Fig. 2) in the casthouse of Century Aluminum's Nordural primary aluminum smelter (Grundartangi, Iceland). In the latter case, liquid aluminum was

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**Fig. 1** LIBS analysis directly in casting launder



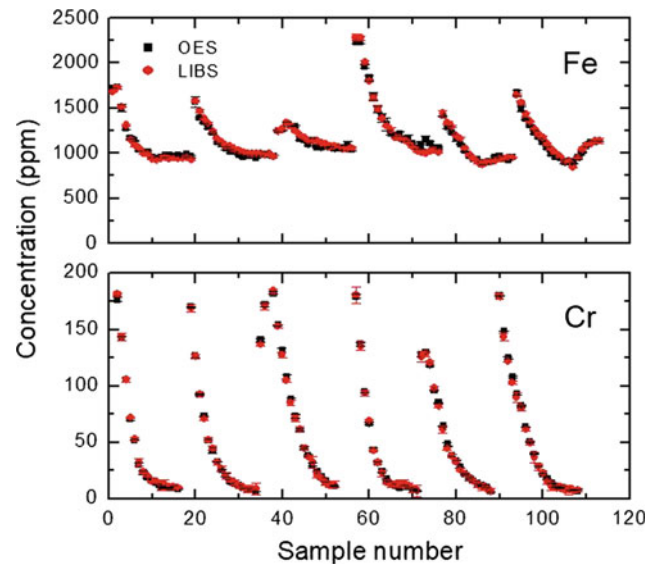
**Fig. 2** Robot feeds sample of liquid Al to LIBS analyzer

extracted by a robot from crucibles and delivered to the DTE-LIBS analyzer, where the melt temperature was regulated and measures were taken to circumvent the effects of surface oxidation. The analyzer was configured to measure up to 14 trace elements, namely Fe, Si, Cu, Ni, Ti, Cr, Mn, Sn, V, Ga, Zn, Sb, Mg and Na. Further measurement details can be found in Ref. [13].

## Results

### Measurement Accuracy

Previously, we have reported on the calibration of the DTE-LIBS analyzer for primary aluminum [13]. In order to establish this calibration, measurements on melts with intentionally added impurities were compared with laboratory OES measurements on corresponding solid samples. Examples of series of measurements for two elements, Fe



**Fig. 3** Comparison of concentration measurements for two representative elements using LIBS analysis of liquid samples and OES spark analysis on corresponding solid samples

and Cr, are shown in Fig. 3, confirming the absolute accuracy of the LIBS analysis after calibration. Using concentration measurements independent of the calibration dataset, it was established that the agreement between the absolute concentration values measured with the two techniques was, on average, within 2–3 ppm for non-volatile elements present in low concentrations (<100 ppm, i.e. Cu, Cr, Mn, Sn, Ni, Ti and V). For the trace elements exhibiting the highest vapor pressure (Zn, Mg, Na, Sb), the comparison with solid reference samples was found to be less reliable. For higher-concentration elements Fe and Si, the agreement between LIBS and OES measurements was found to be within 25 ppm (for absolute concentrations around 1000 ppm and 500 ppm, respectively). In the previous study, limits of quantification (LoQ) for trace elements down to 5–7 ppm were demonstrated. With improvements in sample collection that were applied in the present work, we believe that LoQ as low as 1–2 ppm can be realized for certain elements, although a separate study will be required to confirm this.

### Measurement-to-Measurement Repeatability

The repeatability of LIBS measurements on the same melts was also reported in Ref. [13], showing relative variations between repeated measurements on the same samples of 1–2% in OES and 1–4% in LIBS (for concentrations around 100 ppm in most cases). We report here a comparable study where robotic feeding of molten metal to the DTE-LIBS analyzer was used. Both primary aluminum and AlSi7Mg0.3

alloy melt samples were studied. Prior to LIBS analysis, solid samples of pure aluminum or aluminum alloy were measured using OES (3 or 4 measurements on 3 or 6 nominally identical samples, respectively). The OES measurements were conducted in accordance with the smelter's standard laboratory practices and the average measurement variability between sets of 3 or 4 measurements was determined in the same way as in Ref. [13]. The samples of pure aluminum or alloy were subsequently melted and measured repeatedly using the DTE-LIBS analyzer (3 × 43 or 3 × 42 measurements, respectively). In the LIBS analysis, standard deviation and average were evaluated on each set of 3 measurements, carried out within a period of <1 min).

Table 1 shows the concentration values (OES) and the absolute measurement-to-measurement variation observed for OES and LIBS analysis of the investigated elements in a

sample of primary aluminum. The results show that the measurement-to-measurement repeatability in the LIBS measurement is in most cases similar to or better than in OES measurements on the corresponding process samples, the only major exceptions being V, Sn and Zn. As noted above, the uncertainty in the OES measurement can, to a large degree, be attributed to the sampling process itself [1], while OES measurement repeatability on homogenized standards is, in general, somewhat better.

The difference in repeatability is even more pronounced for alloy measurements. As shown in Table 2, the measurement-to-measurement variation is reduced up to five times for DTE-LIBS analysis, compared to OES results. LIBS measurements exhibited better repeatability than OES results for most of the investigated elements in the alloy samples, the only exceptions being V and Zn, as was also the

**Table 1** Comparison of measurement repeatability for LIBS (liquid) versus OES (solid) analysis for primary aluminum. Na concentration is measured before melting and is therefore only applicable to OES analysis

Element	Concentration (ppm)	$\sigma$ (%) OES	$\sigma$ (%) LIBS	$\sigma$ (ppm) OES	$\sigma$ (ppm) LIBS
Si	327.6	1.7	0.7	5.5	2
Fe	900.3	1.8	1.3	16	12
Cu	9.8	3.0	2.4	0.3	0.2
Mn	7.4	3.1	2.0	0.2	0.1
Ni	43.3	1.8	1.6	0.8	0.7
Cr	4.4	10.7	4.3	0.5	0.2
Sn	1.7	14.8	34	0.2	0.6
Ti	53.5	0.9	1.1	0.5	0.6
V	60.7	0.6	3.4	0.4	2
Ga	100.0	1.4	0.8	1.4	0.8
Sb	30.3	5.0	2.0	1.5	0.6
Na	3.6	31	(34)	1.1	(1.2)
Zn	21	1.6	63	0.3	13

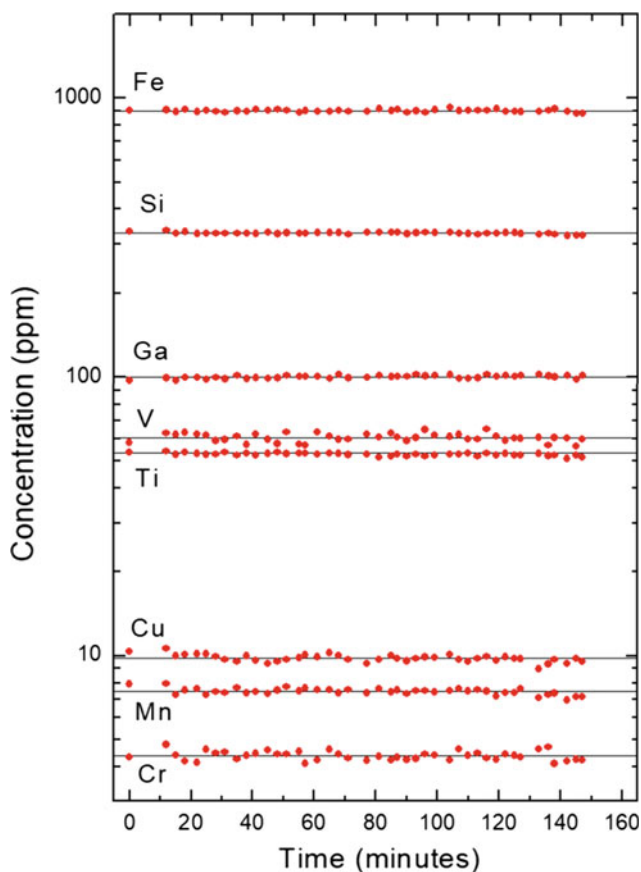
**Table 2** Comparison of measurement repeatability for LIBS (liquid) versus OES (solid) analysis for AlSi7Mg0.3 alloy

Element	Concentration (% or ppm)	$\sigma$ (%) OES	$\sigma$ (%) LIBS	$\sigma$ (ppm) OES	$\sigma$ (ppm) LIBS
Si	7.04%	0.8	0.5	542	383
Fe	1020	2.4	0.7	24	7.2
Cu	11.8	7.3	1.4	0.9	0.2
Mn	31.0	3.4	1.2	1.0	0.4
Ni	58.2	3.9	1.0	2.3	0.6
Cr	12.3	8.4	2.8	1.0	0.3
Ti	1205	1.1	1.0	12.8	11.9
V	122.5	1.3	2.8	1.6	3.5
Ga	82.7	2.3	1.3	1.9	1.1
Na	7.8	13.3	15.6	1.0	1.2
Zn	114.3	1.7	9.5	1.9	10.8
Mg	0.304%	2.8	0.9	86.1	26.0

case for the primary aluminum. In the alloy samples, Sn and Sb were not monitored in the OES analysis and are therefore excluded from the comparison.

## Measurement Stability

The results presented above refer to the internal consistency of a number of measurements carried out during a short time interval. Measurements that show a significant drift over longer time periods may nevertheless still exhibit high internal repeatability. In OES, repeated measurements may, e.g., contaminate or modify the surface in such a way that a large number of measurements on the same sample will not give consistent results, without intermediate surface preparation steps such as milling. In liquid aluminum, however, the surface is not permanently modified by the analysis and therefore shows very high stability of measurement results. This is illustrated in Fig. 4, showing repeated LIBS analysis on the same melt sample, measured every 3–4 min over a period of 2.5 h. For the elements shown in the figure, there is



**Fig. 4** Repeated LIBS measurements on the same melt sample (primary Al). Black lines represent the average measurement values over the full period

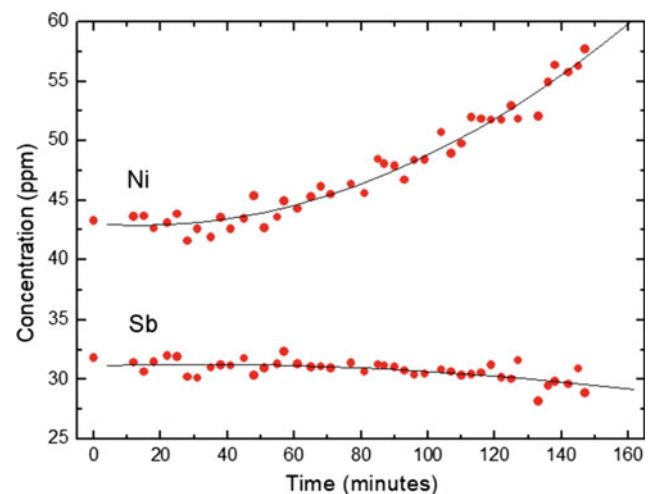
no observable drift in the measurements over this period of time.

In addition, it can be noted that the LIBS-OES concentration comparison mentioned above the DTE-LIBS analysis was carried out over a period of 3 months, without recalibration of the analyzer [13]. Measurement stability has therefore also been confirmed over much longer time intervals.

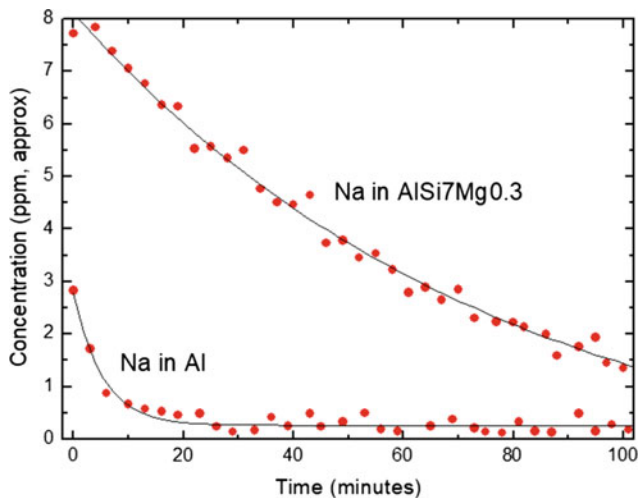
## Real-Time Measurements

Not all elements in the melt exhibit the stability illustrated in Fig. 4. Of the investigated elements, the ones with the highest vapor pressure are (in increasing order) Sb, Mg, Zn and Na [13]. The case of Sb is shown in Fig. 5, where a slight decrease in concentration (approximately 10%) is observed over the 150-min measurement period. On the other hand, the concentration of one element, Ni, was found to increase with time. This can be easily accounted for, however, as the temperature of the melt was monitored throughout the whole measurement period using a K-type (Chromel/Alumel) thermocouple, consisting of >90% Ni. It is well known that this type of thermocouple will dissolve in liquid aluminum with time, consistent with our results.

Concentration changes in the melt can also be more rapid and in those cases, it is more difficult to establish proper correlations between measurements of solid and liquid samples [13]. It is straightforward, however, to monitor relative changes in concentration in the melt, as shown for sodium in Fig. 6. In primary aluminum, the Na concentration drops rapidly in the matter of minutes, as also reported in Ref. [13]. In the alloy melt, however, the sodium



**Fig. 5** Elements changing with time in the primary aluminum melt, as measured by LIBS analysis. Black lines are provided as guides to the eye



**Fig. 6** Sodium concentration, measured by LIBS. An approximate calibration is obtained using the OES-measured Na concentration in the alloy sample prior to melting. Black lines are exponential decay curves

concentration was found to drop more slowly. Both curves are seen to follow approximately a first-order exponential decay, with  $1/e$  decay times of about 5 and 77 min for primary Al and AlSi7Mg0.3 alloy, respectively. This is in line with the results of Ref. [14] where it was found that the rate of sodium evaporation from pure aluminum was approximately one order of magnitude faster than from 12% Si alloy.

## Conclusions

We have shown that LIBS analysis of aluminum and aluminum alloys in their molten state is, for most of the investigated elements, superior to OES laboratory analysis of solid process samples. Furthermore, LIBS measurements can provide an unprecedented level of detail about melt dynamics in real-time. The LIBS analysis reported here was obtained in a fully automated system using robotic feeding, thus eliminating all operator-related errors and sources of uncertainty relating to metal solidification. LIBS analysis therefore offers smelters multiple advantages over current industry practice, including increased information, more rapid feedback, work-hour savings, real-time tracking of

melt composition, improved measurement accuracy, reduced load on central laboratories and improved worker safety.

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