AL29 - Plant-Floor Chemical Composition Analysis of Liquid Aluminum

Kristján Leósson
Chief Scientific Officer, DTE ehf., Reykjavik, Iceland
Corresponding author: kristjan.leosson@dte.ai

Abstract

Recent progress in chemical composition analysis of primary aluminum and aluminum alloys in the liquid state using laser-induced breakdown spectroscopy (LIBS) will be discussed. The company DTE has developed first-in-industry elemental analyzers for plant-floor operation in aluminum smelters. This includes semi-automatic portable analyzers for use in primary aluminum production, and fully automatic stationary analyzers applicable to secondary production and aluminum recycling. Here, the use of portable liquid-metal elemental analyzers for monitoring reduction cells in primary aluminum smelters will be described. Instantly available chemical composition information on the plant floor allows for faster decision making and improved process control. Furthermore, the transfer of data from the portable analyzers to a machine-learning driven data platform has been demonstrated, providing predictive insights, e.g., for reduction of tap-out risk. In addition to process monitoring applications, direct chemical analysis of liquid metal analysis also offers new opportunities in fundamental research into melt dynamics.

Keywords: Aluminum electrolysis, LIBS, Chemical composition analysis of liquid aluminum.

1. Introduction

The aluminum industry relies on chemical analysis throughout the entire production chain, from the electrolysis process through alloying, modification, refining, and recycling. Since the 1970s, spark optical emission spectroscopy (spark-OES) has been the dominant chemical analysis technique in the industry, allowing rapid analysis of multiple trace and alloying elements simultaneously. In spark-OES analyzers, a plasma is induced by electrical breakdown across a small gap between the electrically conductive sample and an electrode. Spark-OES (like other atomic emission spectroscopy techniques) offers only *comparative* analysis and must therefore be standardized against known reference samples, unlike the much more time-consuming *definitive* analysis methods, based mainly on wet chemistry [1].

Another atomic emission spectroscopy technique, developed soon after the invention of the laser in the 1960s, involves inducing a plasma using laser light. It is nowadays typically referred to as laser-induced breakdown spectroscopy (LIBS) [2]. In LIBS analysis, high-energy laser pulses are focused on the surface of a sample, which does not have to be electrically conductive. Laser ablation and laser-induced plasma formation generates atomic (and, in some cases, molecular) optical emission containing chemical information about the sample.

The potential of generating laser-induced plasma for chemical analysis on the surface of liquid metal was realized early on [3], and many pilot projects across different metals industries using LIBS technology have since been conducted [4], including measurements directly on reduction cells [5]. In recent years, DTE has performed extensive validation of LIBS analysis in primary aluminum smelters, using both fully automatic stationary analyzers [6] and semi-automatic portable analyzers [7], confirming that LIBS offers a possibility to transfer chemical analysis for process control out of the laboratory and onto the plant floor, even in the challenging environmental conditions of primary aluminum smelters.

2. Experimental

2.1 Measurement Principle

Chemical analysis of liquid aluminum sampled directly from reduction cells in different smelters was carried out on mobile, battery-powered, and wirelessly connected devices (model number EA-1000), typically mounted on a transport vehicle as shown in Figure 1. The device contains the pulsed laser, high-resolution spectrometer, intensified photodetector, timing electronics, and on-board computer for spectral analysis. Furthermore, the system has built-in sensors for monitoring vibration, magnetic field vector, and internal and external temperatures. Stable system operation has been verified at ambient temperatures up to 45°C and magnetic field strengths exceeding 200 Gauss (20 mT).

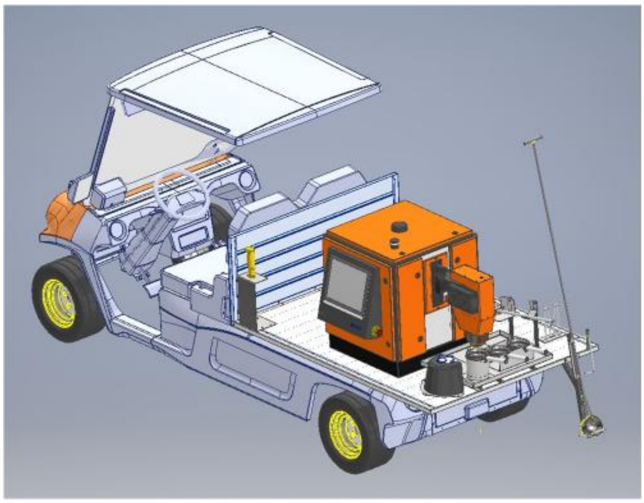

Figure 1. Portable LIBS analyzer mounted on a transport vehicle.

The swivel-mounted measurement head contains a Nd:YAG Q-switched laser module and focusing optics. Before measuring, the head closely approaches the liquid metal surface. In DTE's EA-1000 model portable LIBS analyzer, a measurement is performed by 70 laser pulses of ≈100 mJ pulse energy impinging on the liquid metal surface at a 20 Hz repetition rate (measurement time 3.5 seconds). The resulting plasma emission is collected and transmitted via optical fiber to the high-resolution spectrometer, where it is dispersed and accumulated using an intensified CCD detector. The combination of high spectral resolution and high detector sensitivity ensures that emission signals from individual elements are efficiently separated and detected even at ppm-level concentrations.

Figure 2 illustrates a section of a LIBS spectrum collected by an EA-1000 analyzer, measuring aluminum collected directly from a reduction cell. Although the section shown in the figure covers only a small part of the UVC wavelength range (less than 1% of the full spectrum collected by the device), it contains many emission peaks that can be used for quantification of Si and Fe in the liquid metal sample. Other sections of the spectrum will contain information about additional elements of interest. The recorded spectrum matches well a calculated spectrum based on tabulated properties of the respective atomic energy levels and transitions [8], using typical values of plasma temperature of 8000 K and an electron density of 5×10^{16} cm^{-3} for the calculation [9], and the expected spectral resolution of the detection system Following standard spectroscopic notation, the calculated emission peaks of neutral atoms are labeled I, while emission peaks from singly ionized atoms are labeled II.

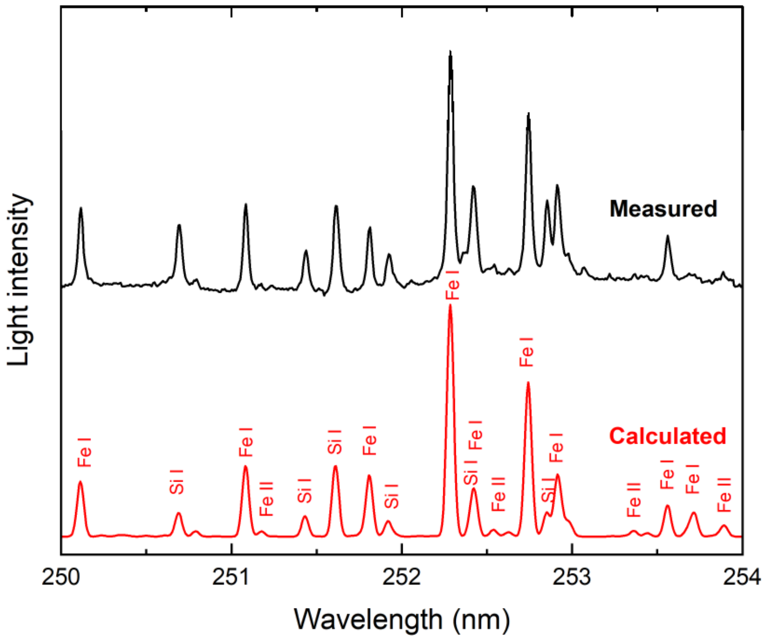

Figure 2. Section of recorded LIBS spectrum from primary aluminum (black line) and a simulated spectrum (red line) where the (molar) concentration of Fe was taken as being 10x higher than that of Si. The spectra are vertically offset for clarity.

As in the case of spark-OES, quantification in LIBS analysis is realized by establishing calibration functions for converting spectral intensities to chemical composition. For the liquid-metal LIBS analysis, such calibration functions are constructed by measuring a series of samples of liquid metal with known concentrations of the impurities and/or alloying elements of interest. In this way, devices are factory-calibrated to cover specific elements and concentration ranges. In operation, devices display the concentration values for the installed elements immediately after the measurement is completed and the chemical analysis data can be transmitted wirelessly to the process management systems.

2.2 Plant Operation

The sequence of operations for measuring aluminum from a series of reduction cells is shown in Figure 3. The operator extracts a sample of liquid aluminum in a conventional fashion and pours it into a measurement ladle (Figure 3a). At the press of a button, the device initiates the measurement sequence, which involves optically monitoring the temperature of the liquid metal as it cools, such that the LIBS measurement is performed (Figure 3b) within a consistent range of melt temperatures. Measurements are advantageously performed under argon flow (or a mixture of argon and an atmospheric gas component [10]) provided from a pressurized cylinder mounted on the transport vehicle. A 5L cylinder at 200 bar holds enough gas for approximately 2000 measurements. After the measurement, the measurement ladle is detached, and the liquid metal can be discarded (Figure 3c). The transport vehicle is then moved to the next cell. On some models this can be done with an external driving mechanism (Figure 3d).

In normal operation, the full measurement sequence – including moving of the transport vehicle between reduction cells – can be completed in about 70 seconds, meaning that chemical analysis can be obtained from 40 reduction cells in about 45 minutes by a single well-trained operator, assuming that access to the liquid aluminum through the crust is ensured. DTE’s patent-pending approach for portable LIBS analysis of liquid metal ensures that repeatable results can be obtained in a rapid fashion when measuring multiple reduction cells in sequence [11].

Figure 3. Chemical analysis of liquid aluminum from reduction cells.

The device display provides the recent history of analysis from each reduction cell, and it can be configured to provide automatic warnings if an anomalous increase in concentration is detected. If, for example, an increase in Fe concentration is detected the device can be configured to request a retry with a newly coated extraction ladle, to rule out ladle contamination. Anomalous changes in concentration of specific elements can be acted on immediately.

2.3 Device Calibration

As discussed above, the LIBS analyzers are factory-calibrated to cover certain elements and concentration ranges, analogous to conventional laboratory devices such as spark-OES analyzers. For mobile analytical devices operating in harsh environments, however, it is critical to ensure that operation remains stable, despite vibrations, temperature fluctuations, dust, fumes, strong magnetic fields, and other environmental factors. Certain components of the EA-1000 analyzer, including the spectrometer, are regularly self-calibrating. The analytical performance of the analyzer can be monitored by periodically measuring solid control samples to ensure that readings remain stable. Also, the samples of liquid metal measured with the LIBS analyzer can be cast into conventional sampling molds for off-line analysis using trusted techniques.

If needed, the factory calibrations can be adjusted using proportional correction factors for each element. Unlike systems that have physical spectrometer slits and individual photodetectors for each recorded emission line, it is not necessary to use a second (offset) parameter for standardization of calibration curves in the LIBS analyzer, because the full spectral detection (Figure 2) makes dynamic background subtraction possible. Furthermore, the fact that plasma generation is realized without the use of a physical electrode in the LIBS analyzer means that standardization is required much less frequently than on spark-OES systems. In many cases, the molten-metal LIBS analyzers have been operated in plant settings for weeks or months without standardization or recalibration.

3. Results and Discussion

3.1 Analytical Performance

To date, DTE’s portable LIBS analyzers have been used mainly for regular monitoring of Fe, Si, Cu, and Mn concentration levels in reduction cells, although results for additional elements have also been reported previously [7]. For LIBS analysis of liquid metal, the upper limit of measurable concentration is given by the solubility of each element in the aluminum. Above this limit, formation of solid phases in the melt may impact the LIBS measurement, but below the solubility limit the LIBS analysis is generally highly repeatable, even at concentrations where measurements of solidified material become unreliable [9]. For binary alloys above the melting point of pure aluminum, the solubility limit is over ≈2 wt% for Fe and Mn, while for Si it is above ≈20 wt% and for Cu above ≈60 wt%. On the low concentration side, the limit of quantification (LoQ) for the LIBS analysis depends on the element being measured, as well as on the measurement configuration.

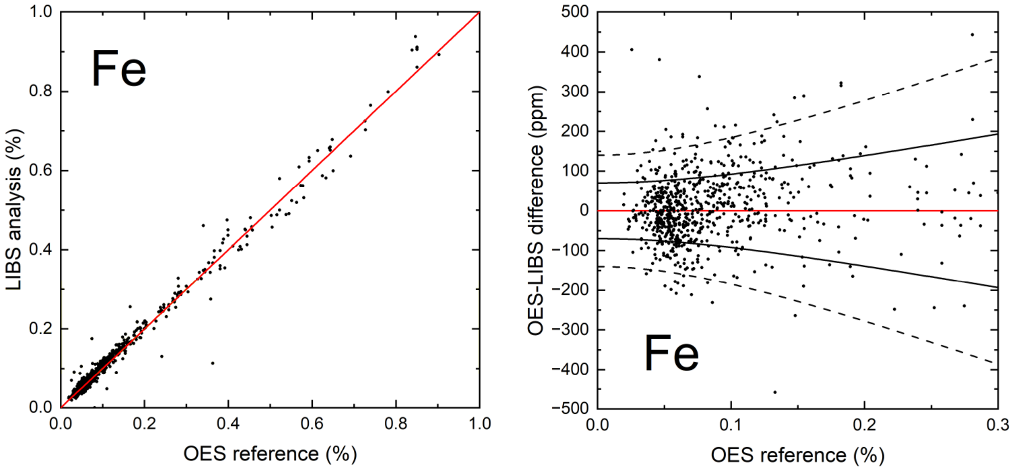

Figure 4. Left: LIBS analysis of Fe in approximately 800 samples of molten aluminum from reduction cells, measured in different smelters, compared to spark-OES analysis of solid samples cast from the same melt. Right: difference between the two analysis methods for the lower part of the measurement range. Black solid and dashed lines show ±1σ and ±2σ of the distribution, respectively.

Figure 4 (left) shows measurements performed on metal samples extracted from different reduction cells over the course of several weeks (approximately 800 samples in total). Data from different smelters is combined. Approximately 10 % of the data points represent Fe concentrations above 2000 ppm, but reduction cells with high levels of Fe were sampled disproportionately more frequently, to verify the results across the full calibrated range of up to 1 wt% Fe. The distribution of data points in Figure 4, therefore, does not represent the actual distribution of Fe levels between cells in the smelters.

The level of agreement between LIBS analysis on the molten metal and the spark-OES analysis on corresponding solid samples is further illustrated in Figure 4 (right) where the difference of LIBS and OES results for samples from reduction cells having Fe concentration below 0.3 wt% is shown as a function of the Fe concentration. The distribution of points around y = 0 can be characterized by the standard deviation of the calculated differences, which in this case was equal to 75 ppm. For higher Fe concentrations, an additional component of uncertainty proportional to the measured concentration can be added. For Fe concentrations above 3000 ppm, 68% of data points (±1σ) fall within ±6% of the measured concentration.

The agreement between the LIBS and spark-OES results depends on the combined measurement uncertainties of both devices. The combined uncertainty shown in Figure 4 is of the same order as the combined uncertainty of two spark-OES devices used to measure the same set of solid samples collected from reduction cells. Such a test, involving 185 samples in the Fe concentration range 550–3000 ppm, gave a standard deviation of differences between measurements on two spark-OES devices of 57 ppm and for higher concentrations (up to 1 wt% Fe) the agreement (±1σ) was within 7 % of the measured concentration. These numbers will, of course, depend on the sampling procedures, and the types of spark-OES devices used, their standardization, and the number of sparks made on each sample, but the numbers above are believed to be representative of standard conditions and analysis procedures in the industry. For comparison, it can be pointed out that the agreement in Fe measurements between different OES laboratories in ASTM interlaboratory testing is of the order of 2.5 % (1σ) for Fe concentrations of 0.3–0.5 wt%, for high-quality reference samples (6000-series alloy) [12].

The limit of quantification of for the portable LIBS analyzer can be taken to be of the same order as the distribution of differences as the concentration approaches zero, i.e., approximately 70 ppm for Fe in the present case (Figure 4). Similar analysis can be made for the other elements of interest, as listed in Table 1. The results from the present tests on 800 samples measured in industrial settings are comparable to previously published data, collected with a single prototype device and involving a much smaller data set (n=56). By comparison, stationary analyzers can offer lower quantification limits and are typically calibrated for more elements and wider concentration ranges, suitable also for characterization of aluminum alloys.

Table 1. Parameters of portable LIBS devices for analyzing metal from reduction cells.

Element	**Estimated LoQ (ppm)**	**Typical calibrated range (wt%)**	**Theoretical maximum range (wt%)**
Fe	70	1	> 2
Si	20	0.2	> 20
Cu	2	0.02	> 60
Mn	5	0.02	> 2

3.2 Utilization of Real-Time Information

Using conventional sampling and analysis technology, delay times between sampling of reduction cells and receiving analysis results from centralized laboratories are typically measured in hours. Conversely, as pointed out above, having access to real-time chemical analysis enables real-time decision making on the plant floor. Furthermore, the analysis data can be immediately transferred from the LIBS device to a plant control system, ensuring that plant managers have access to the most up-to-date information at each time. DTE provides such a system (IREAS platform) to provide an overview of the status of the smelter. An example for a hypothetical smelter is shown in Figure 5.

To provide warnings to operators, the system can use hard chemical composition limits or other pre-programmed user-defined conditions. More usefully, however, a machine-learning model [13] provides future-looking risk scores based on the chemical composition data, as well as other parameters such as cell age. Optimum performance of such a model is obtained by training the model on historical data of chemical composition and fate of individual pots in the particular smelter. The platform can provide a visual aid to plant management in determining which reduction cells need specific attention, days or weeks before a potential incident.

Figure 5. Example screen from DTE's IREAS platform for a hypothetical smelter.

The platform also provides tools for verification of the stability of the LIBS analyzers, including historical data of solid control samples measured with the analyzers, as well as correlation with comparison samples measured using other analysis methods. Furthermore, the environmental and operating parameters tracked by individual LIBS analyzers being used by the plant can be monitored remotely in the platform.

An analysis of potential profitability of implementing real-time chemical analysis and the data processing platform has been presented elsewhere, indicating a potential 1.5-4 % increase in profitability in primary aluminum smelter, mainly due to reduced operational costs [14].

4. Conclusion

Chemical analysis of molten metal performed in situ promises to radically change process control in the aluminum industry. Analytical performance of LIBS-based molten metal analyzers matching that of current industry practices has been demonstrated for elements of interest. This includes portable LIBS analyzers for monitoring the chemistry of aluminum from reduction cells. Moving the responsibility of chemical analysis from the laboratory to the plant floor and making use of real-time data collection and dynamic data analysis presents new opportunities but also requires organizational changes to extract maximum operational value for the smelter.

5. References

1. Thomas R. Dulski. *A Manual for the Chemical Analysis of Metals*, West Conshohocken PA, American Society for Testing and Materials (ASTM), 1996, 251 pages.
2. Jagdish P. Singh, Surya N. Thakur, eds., *Laser-induced breakdown spectroscopy*, 2nd edition, Amsterdam, Elsevier, 2020, 454 pages.
3. E.F. Runge, S. Bonfiglio, F.R. Bryan, Spectrochemical analysis of molten metal using a pulsed laser source, *Spectrochimica Acta*, Vol. 22, No. 9 (1966), 1678-1680.
4. Ashwin .K. Myakalwar et al., LIBS as a Spectral Sensor for Monitoring Metallic Molten Phase in Metallurgical Applications – A Review, *Minerals* Vol. 11, No. 10 (2021), 1073.

5. Lanxiang Sun et al., Applications of laser-induced breakdown spectroscopy in the aluminum electrolysis industry, *Spectrochimica Acta Part B*, Vol. 142 (2018), 29-36.
6. Sveinn H. Gudmundsson, Halldor Gudmundsson, Kristjan Leosson, Automated Chemical Analysis of Liquid Aluminum for Process Control, *Light Metals* 2021, 758-762.
7. Sveinn H. Gudmundsson, Birna Björnsdóttir, Kristjan Leosson, Instant Monitoring of Aluminum Chemistry in Cells Using a Portable Liquid Metal Analyzer, *Light Metals* 2021, 491-494.
8. Alexander Kramida, Yuri Ralchenko, Joseph Reader, and NIST ASD Team, *NIST Atomic Spectra Database*, ver. 5.10, Gaithersburg MD, National Institute of Standards and Technology, 2022.
9. Kristjan Leosson et al., Analysis of dissolved titanium concentration and phase transformation in molten Al-Ti alloy using laser-induced breakdown spectroscopy, *Spectrochimica Acta Part B*, Vol. 190 (2022), 106387.
10. Kristjan Leosson, Kristbjorg A. Thorarinsdottir, Kristinn Benediktsson, DTE ehf., *Patent Application* EP23166791.6, filed Apr. 5, 2023.
11. Sveinn H. Gudmundsson, Kristjan Leosson, DTE ehf., *Patent Application* WO2023037392A2, filed Sept. 8., 2021.
12. Committee E01 Proficiency Test Program Chemical Analysis Aluminum, May 2021. *ASTM International PTP Office*, Report issue date Sept. 7, 2021.
13. Rauan Meirbekova, Sveinn H. Gudmundsson, Kristjan Leosson, Portable Elemental Analysis Device for Real-Time Chemical Analysis, *Proceedings of the 39th International ICSOBA Conference*, Virtual, 22-24 November 2021, Paper AL 38, *Travaux* 50, 1013-1020.
14. Berglind Höskuldsdóttir, Karl A. Matthiasson, and Pall Jensson, Profitability Increase in Aluminium Smelter Potroom Using Real-Time Elemental Analysis from Liquid Metal Based on LP-LIBS, *Proceedings of 39th International ICSOBA Conference*, Virtual, 22-24 November 2021, Paper AL 37, *Travaux* 50, 1021-1028.