

## Automatic Real-Time Chemical Composition Analysis (LP-LIBS) in Casthouse Operations

Kristjan Leosson<sup>1</sup> and Berglind Hoskuldsdottir<sup>2</sup>

1. Chief Technical Officer

2. Product Manager

DTE, Reykjavik, Iceland

Corresponding author: kristjan.leosson@dte.ai

<https://doi.org/10.71659/icsoba2024-ch008>

### Abstract

Knowledge of chemical composition is important at multiple stages of smelter operations. At the electrolysis stage, impurities in the molten metal reveal the state of the reduction cells and the quality of raw materials. Further downstream, chemical analysis is crucial for monitoring the melt composition at the stages refining and alloying, and for maximizing the value of final smelter products. DTE has successfully implemented fully automated chemical analysis of the molten metal in primary and secondary casthouses, analysing metal from transport crucibles as well as furnaces, where real-time, minute-by-minute chemical information of the molten metal can assist in optimizing furnace operations. The performance of those plant implementations will be discussed, including analysis accuracy, concentration ranges, and long-term stability. DTE's solution combines the connected analysers and an online cloud platform, IRIS, transforming the real-time chemical analysis results, along with other process data, into predictive insights and actionable information, leading to process improvements and increased operator safety. DTE recently supplied four automatic crucible analysis solutions to a primary aluminium smelter in Iceland. The automated systems are a crucial part of the metal treatment process for transporting crucibles in the smelter's new billet casthouse. Having precise chemical composition information from the crucibles is essential for efficient furnace quality control during the alloying process. DTE's solution was also integrated into a recycling furnace at a secondary aluminium production plant, now offering the customer real-time information on batch composition. This opens up opportunities to enhance furnace operation, increase throughput and optimize feedstock.

**Keywords:** LIBS, Chemical composition analysis of liquid aluminium, Casthouse process control, Industry 4.0, Process automation.

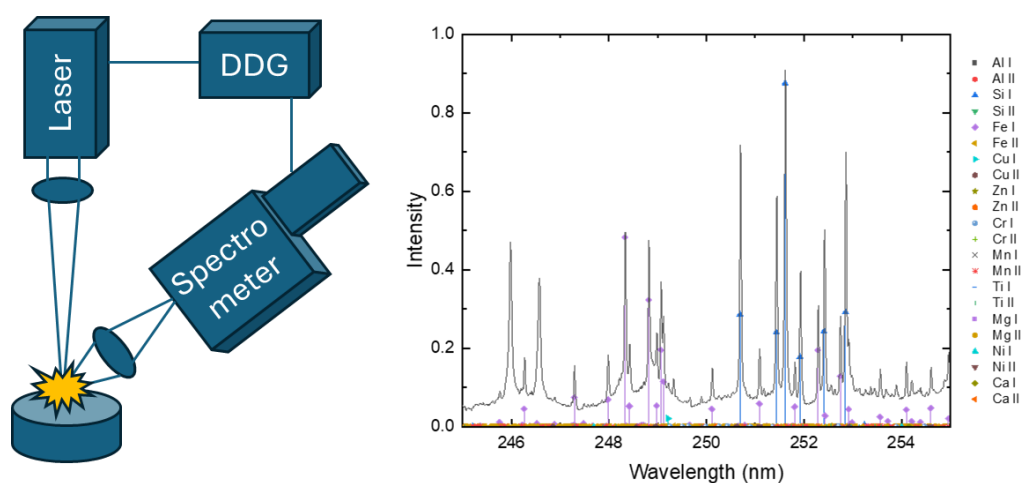
### 1. Introduction

Monitoring alloy chemistry during production has typically involved manually extracting molten metal from different points in the production process and casting it into solid samples for laboratory analysis. For chemical analysis, the industry has mainly relied mainly on spark optical emission spectroscopy (spark-OES), where electrical breakdown is induced in a small gap between the solid metal sample and a high-voltage electrode. The spectral fingerprint of the optical emission from the spark plasma is characteristic of the constituent elements of the sample [1].

In the early 1960s, three years after the invention of the laser, researchers at the Ford Motor Company realized that this novel device, operated in a high-energy pulsed mode, could be used to generate a plasma at the surface of a solid or molten metal [2]. They stated: "The possibility of determining the chemical composition of a material situated in a hostile environment, such as molten metal within a furnace, by a method which does not require the removal and cooling of the sample, has long intrigued both melters and analysts. The practicality of performing such an

analysis by means of a laser has been conjectured by the authors since finding, in 1963, that a laser can excite useful spectra from solid metals without an auxiliary electrical discharge.”

Around the turn of the century, following improvements in pulsed laser sources, fast and sensitive photodetectors, and compact high-resolution spectrometers, this field of chemical analysis, now commonly referred to as laser-induced breakdown spectroscopy (LIBS), started growing rapidly [3]. The basic principle is still the same as that envisioned by the researchers at Ford Motor Company, i.e., the simultaneous ablation and excitation of material, typically using the focused beam of a pulsed laser, with subsequent detection of the spectrally resolved plasma emission for identifying and quantifying the constituent elements of a sample. Detection limits with this technique have improved by orders of magnitude and have routinely been shown to be in the range of parts per million (ppm) or even lower. As predicted, this method of chemical analysis has proven especially useful in hostile environments – a few LIBS systems have even been sent to Mars to analyze its soil chemistry [4]. The basic principle of the LIBS measurement is illustrated in Figure 1.



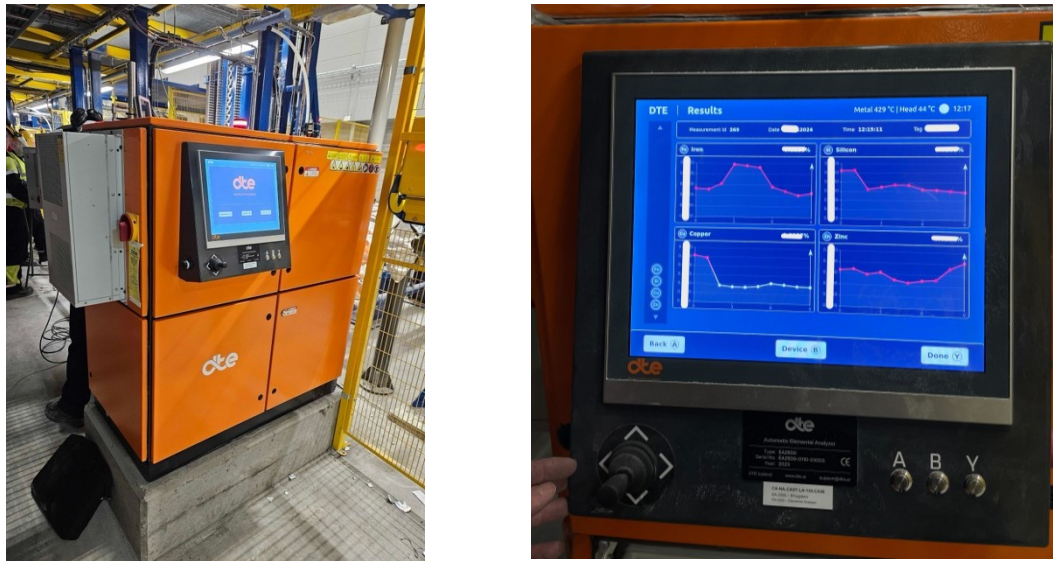
**Figure 1. Basic principle of the LIBS analysis method: A pulsed laser beam is focused onto the surface of the sample (e.g., liquid aluminium) to ablate a fraction of the sample and convert it into a plasma. The resulting plasma emission is dispersed and detected using a spectrometer, synchronized with the pulsed laser using a digital delay generator (DDG). Specific peaks in the emission spectrum are associated with different elements and used for quantification.**

In recent years, LIBS-based chemical analysis of molten metal has also made its way into metals production [5]. Performing chemical analysis directly on the molten metal offers several advantages, especially when the analysis can be fully automated. This allows for more frequent analysis with immediate results, enabling closer monitoring of changes in melt chemistry, e.g., during alloying or to monitor the uniformity of melt composition during casting. Measuring the liquid metal directly avoids issues that can affect the precision and accuracy of analysis results when preparing solid samples. These issues include inhomogeneous solidification, improper machining, contamination, or sample mix-up [6]. Additionally, the safety of plant workers is improved as they are no longer required to manually extract and handle samples of molten metal.

## 2. Implementations in the Aluminium Smelter Casthouses

The implementation of portable LIBS-based analyzers for potroom operations has been discussed previously [7]. The present paper focuses on fully automated casthouse implementations, such as

the analysis of metal from transport crucibles involving robotic extraction of metal and subsequent automated chemical analysis, as shown in Figure 2. In this scenario, molten metal is sampled and analysed during transport from the potroom to the casthouse of a primary smelter, before and/or after melt treatment in the crucible. The main purpose of this analysis is to check impurity levels to ensure that ladles are routed to suitable furnaces for casting. The impurities of interest in this case are primarily Fe, Si, Cu, Zn, and Na, present in relatively low concentrations. Depending on external conditions, automated analysis of melt chemistry in transport crucibles can be set up using a single-robot or two-robot solution, with or without a heating unit to maintain the sample temperature during measurement.



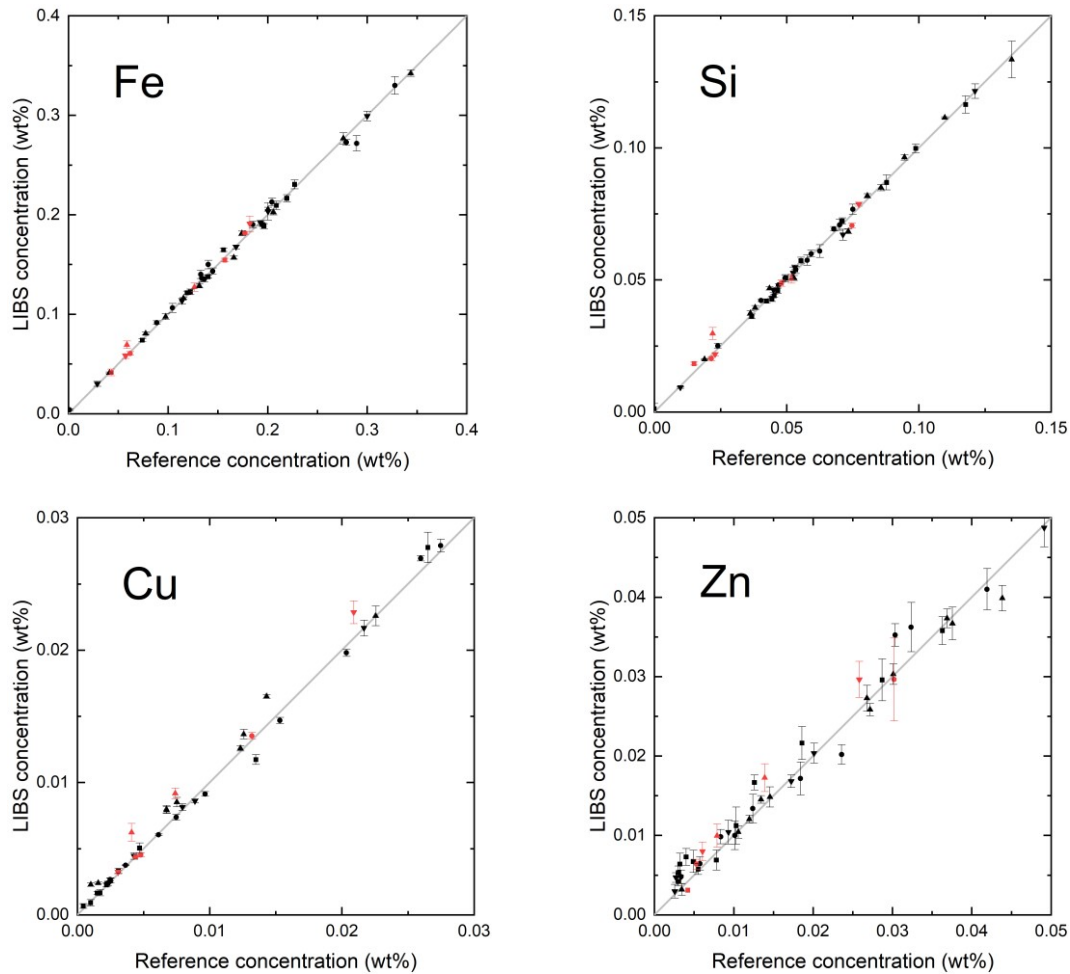
**Figure 2. Left: LIBS analyser positioned at an automated crucible skimming and sampling station, Right: Analysis from a series of transport crucibles (customer data blocked).**

Another example discussed below involves sampling from furnaces equipped with a side well that allows robotic extraction of the metal. In this case, semi-continuous measurements of the furnace's chemical composition can be conducted by repeatedly extracting a sample of molten metal that can be returned to the furnace after analysis. Full cycle time in such cases, can be as short as 5 minutes. For recycling or alloying furnaces, a wider range of elements is typically measured across a broader composition range compared to primary metal cases. DTE's analyzers have been configured to measure various elements in molten aluminium, including Si, Fe, Mn, Mg, Cu, Zn, Ti, Cr, Ni, Sb, Sn, Sr, V, Zr, Na, Ca, Pb, Ga, and Co, with the ability to detect other elements as well. The measurable composition generally ranges from ppm levels (sub-ppm for some elements, 10s of ppm for others), up to the solubility limit of the element in the melt, which may vary depending on the melt temperature.

### 3. Device Calibration, Crucible Analysis

The molten metal LIBS devices are factory-calibrated by preparing a series of 300-500 g melt samples with different chemical compositions. A portion of each melt sample is cast into a solid sample, using conventional procedures and measured with a trusted reference method that is standardized using certified reference materials, such as spark-OES, XRF or ICP. Figure 3 shows examples of such factory-calibration data for Fe, Si, Cu, and Zn, respectively, in concentration

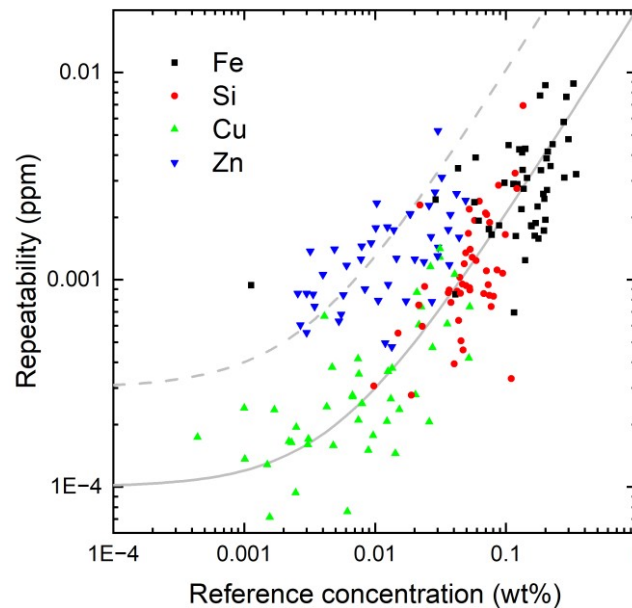
ranges relevant to the analysis of primary metal in transport crucibles. It is worth noting that for analysing primary metal from individual reduction cells, wider concentration ranges are typically applicable, e.g. up to 1 wt% for Fe [7]. The quality of the calibration can be expressed in terms of its correlation coefficients (Pearson R) or the confidence interval of the calibration function. Both will depend on the number and distribution of calibration data points across the composition range in question and on the measurement repeatability. The observed correlation coefficients were 0.996–0.999 for Fe, 0.998–0.999 for Si, 0.992–0.999 for Cu, and 0.984–0.999 for Zn. The confidence limits will vary across the concentration range, but in the cases shown in Figure 3, the average half-width of the 95 % confidence interval is around 50 ppm for Fe, 30 ppm for Si, 10 ppm for Cu, and 20 ppm for Zn.



**Figure 3. Calibration data (black symbols) and independent test samples (red symbols) relevant for analysis of primary aluminium in transport crucibles. Note the different concentration ranges on the x-axes. Different symbol shapes signify data recorded on four separate devices installed at a customer site.**

During the calibration process, each melted sample was analyzed multiple times by the LIBS analyzer, with the recorded variance shown by error bars. During measurement, the samples were maintained at a temperature of approximately 710 °C using an induction heater. For the non-volatile elements Fe, Si, and Cu, the repeatability follows a consistent pattern, as depicted in Figure 4. In the current device and measurement set-up, repeatability can be generally expressed as 2 % of the measured concentration plus 1 ppm, represented by the solid grey line in the figure. The variance in the measurement for Zn is higher, averaging about 10 % of the measured

concentration plus 3 ppm, shown by the dashed grey line in the figure. This behaviour is typical of volatile elements in the melt [8] making their measurement more susceptible to external factors, such as temperature and melt chemistry, as has been extensively studied in the case of Mg [9, 10].

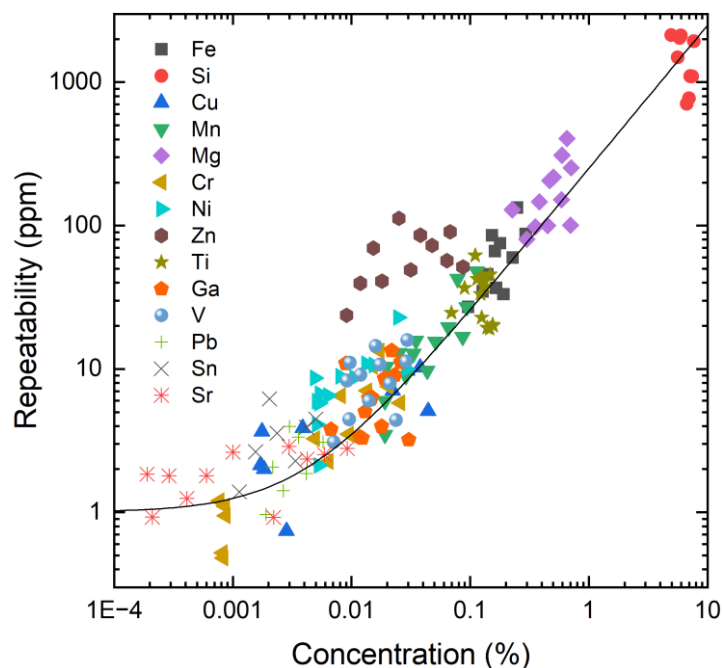


**Figure 4. Measurement repeatability, primary metal. Grey curves represent 1 ppm + 2 % of the measured concentration (solid) or 3 ppm + 10 % of the measured concentration (dashed).**

In the case of sodium (Na), the volatility in primary aluminium is so high that repeated measurements of the same 300–500 g melt sample are not expected to give constant results, as the concentration of Na is expected to drop rapidly [8, 11]. Data for sodium has therefore not been included in Figures 3 and 4. Similarly, extracting and pouring liquid metal from a transport crucible into a sampling mould will result in a lower measured Na concentration in the solid sample than in the crucible. Nevertheless, by comparing individually extracted samples with single LIBS measurements, a correlation can be made between the results obtained from analyses in liquid and solid.

#### 4. Furnace Operation

Molten metal can be sampled from side-well furnaces in a similar fashion as from transport crucibles, using a robot arm to extract a sample of liquid metal that can be subsequently measured by LIBS and/or cast into a solid sample for reference and storage. In furnace operations, the number of elements to be measured and their concentration ranges are typically much larger than when characterizing primary metal. Figure 5 shows LIBS measurement repeatability for samples representing compositions close to typical casting alloys. Fourteen elements were measured simultaneously, ranging in concentrations from 2 ppm to 10 wt%. As in Figure 4, the repeatability follows a common relationship, with the exception of Zn at concentrations below 0.1 wt%, which shows a higher measurement variance. For higher Zn concentrations, the measurement repeatability was found to be closer to that of the non-volatile elements and 7000-series alloys having Zn concentrations up to 7 wt% have been successfully analyzed, in addition to 3000, 5000, and 6000-series alloys.



**Figure 5. Measurement repeatability, casting alloy.**  
**Measurements were performed at a melt temperature of 730 °C.**

It is important to note that the repeatability of Mg measurements in Figure 5 follows the same relationship as the other (non-volatile) elements, despite its high vapor pressure and the strong dependence of the LIBS signal on melt temperature and melt chemistry [9, 10]. This is achieved using DTE's proprietary stable-LIBS™ technology, which ensures that magnesium in the melt can be reliably and accurately measured, even up to the 3–5 wt% levels used in most 5000-series alloys.

An example of time profiles that can be obtained using semi-continuous LIBS analysis is shown in Figure 6, simulating furnace operations on a small scale, and displaying hypothetical target concentrations for Fe, Si, Cu, Mn, and Mg. Initially, a mixture of profile and UBC scrap was melted after delacquering the UBCs at 500 °C. This was followed by the addition of clean sheet metal scrap after 15 minutes, resulting in a modest increase in Mg. Next, pure Mg was added, intentionally overshooting the target, as the Mn concentration was still above its target concentration. The melt was subsequently diluted with primary (smelter-grade) aluminium, before finally adding pure Si to meet the target concentration of around 1 wt%. In an actual furnace operation, the time constants and order of actions will certainly be different, but this example illustrates the general principle of the level of information that can be achieved in real time using automated LIBS analysis, without any operator involvement.

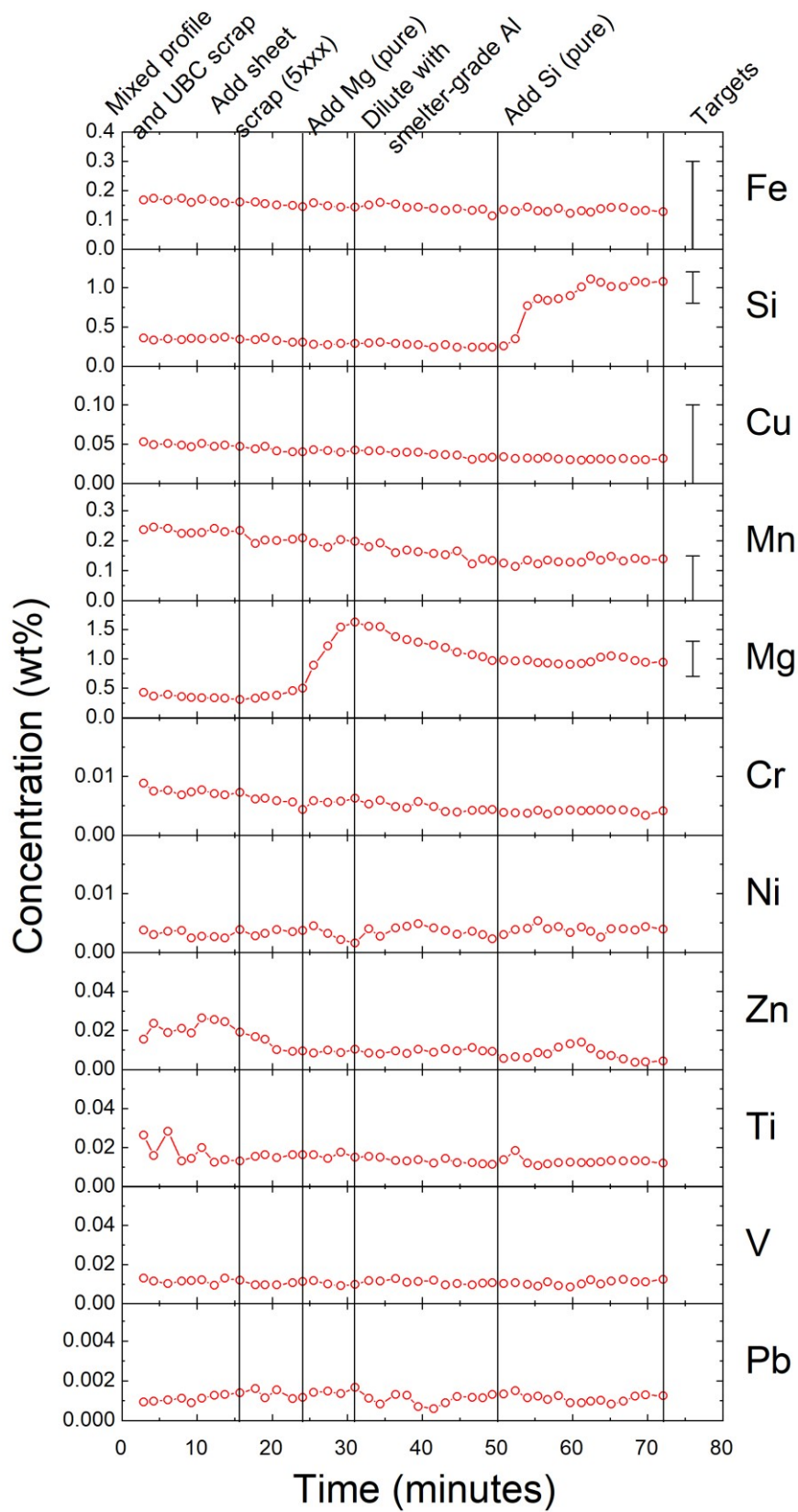


Figure 6. Measured data from a small batch of molten metal, mimicking a hypothetical recycling and alloying process.

## 5. Real-time Process Control

With conventional sampling in aluminium production, an operator typically extracts a liquid metal sample, casts it into a mould, cools it, and transports it to a laboratory for composition analysis. This process generally takes tens of minutes or even hours to obtain the analysis results, depending on the processes at each production facility. In contrast, DTE's LIBS analyzers provide chemical analysis in a matter of seconds, creating new opportunities for real-time process control. To support this, DTE has developed an online cloud platform, IRIS, with multiple features and functionalities that can complement customers' existing production and operations systems. For transport crucibles, IRIS receives the automatically generated chemical analysis result and compares it with set limits for each crucible, as shown in Figure 7. When producing alloys with critical chemistries, crucibles can then be automatically directed to the proper furnace, based on the desired specifications.

The IRIS furnace module monitors batch composition data and compares it with target specifications, alerting in real time if the batch is heading out of specifications. This leads to faster response time and production improvements. Additional IRIS features include correlation with solid comparison samples to verify the stability of the analyzers over time. IRIS also provides a portal for remote device supervision, which includes monitoring operational sensor data, quality of recorded spectra, measurement statistics, and installed calibrations.

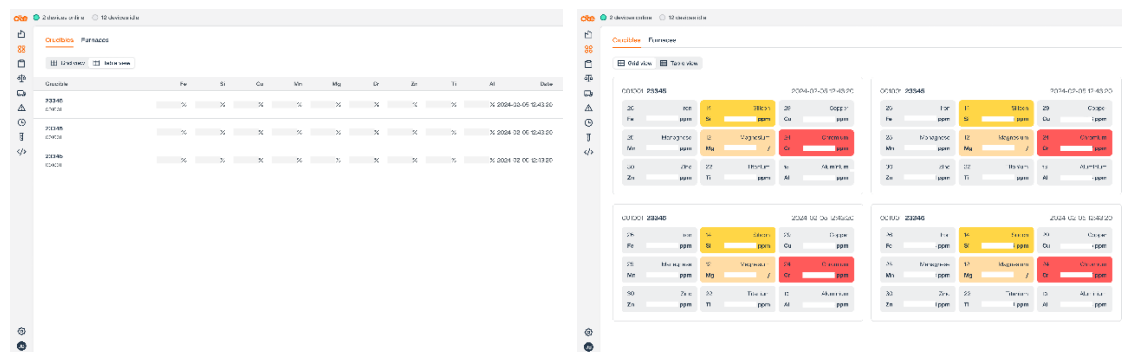


Figure 7. Crucible routing feature in IRIS (customer data blocked).

## 6. Conclusions

We have presented the performance characteristics of industrial LIBS-based chemical analyzers for the aluminium industry. Performing chemical analysis directly on the molten metal has multiple advantages, especially when such analysis can be fully automated. Analysis can be performed much more frequently and with immediate results, which allows for faster decision making and closer monitoring of changes in melt chemistry.

Improved insights into the alloying process from minute-by-minute chemical analysis help operators optimize their alloying process to reduce the time needed in the furnace. Likewise, the need for remelting is minimized by ensuring that the melt is within specifications when cast. Additionally, when recycling streams are used as input, better knowledge of melt chemistry allows margins for recycled material to be increased. This results in energy savings and better use of material resources, consequently, reducing the carbon footprint of alloy production.

The authors respectfully acknowledge the work of the whole DTE team and the company's research collaborators.

## 7. 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. E.F. Runge, S. Bonfiglio and F.R. Bryan, *Spectrochimica Acta*, Vol. 22 (1966), 1678-1680.
3. Vincenzo Palleschi, Forty years of laser-induced breakdown spectroscopy and laser and particle beams, *Laser and Particle Beams*, Vol. 2023 (2023), 2502152.
4. Guobin Jin et al., A new spectral transformation approach and quantitative analysis for MarSCoDe laser-induced breakdown spectroscopy (LIBS) Data, *Remote Sensing* Vol. 14 (2022), 3960.
5. Ashwin K. Myakalwar et al., LIBS as a spectral sensor for monitoring metallic molten phase in metallurgical applications – A review, *Minerals* Vol. 11, (2021), 1073.
6. Thomas Belliveau et al., Using guard bands to accommodate uncertainty in the spark AES analysis of aluminium or aluminium alloys when determining compliance with specified composition limits, *Light Metals*, 2017, 279–287.
7. Kristjan Leosson, Plant-floor chemical composition analysis of liquid aluminium, *Proceedings of 41<sup>st</sup> International ICSOBA Conference*, 6-9 November 2023, Dubai, UAE, Paper AL29, *Travaux* 52, 1509–1516.
8. Sveinn H. Gudmundsson et al., Quantitative in-situ analysis of impurity elements in primary aluminium processing using laser-induced breakdown spectroscopy, *Spectrochimica Acta B*, 158, 105646 (2019).
9. Kristbjörg A. Thorarinsdóttir, Mehdi Maghsoudi and Kristjan Leosson, Vapor-phase contribution to laser-induced plasma emission of magnesium in liquid aluminium, *Applied Spectroscopy*, 78, (2023), 67–75.
10. Mehdi Maghsoudi et al., The influence of alloying elements on Mg vapor pressure in liquid ternary aluminium alloys studied by laser-induced breakdown spectroscopy, *Metallurgical and Materials Transactions A*, 20 June 2024, <https://doi.org/10.1007/s11661-024-07468-8>.
11. Sveinn H. Gudmundsson, Jón Matthiasson and Kristjan Leosson, Accurate real-time elemental (LIBS) analysis of molten aluminium and aluminium Alloys, *Light Metals*, 2020, 860-864.