AA28 - LIBS – An Emerging Technique of Real-Time Elemental Analysis for Process Control in Alumina Production

Alexander Baryshnikov[1], Vitaliy Ovcharenko[2] and Mindaugas Dailidė[3]
1. CTO, PhD, Lyncis UAB, Vilnius, Lithuania
2. Innovation Director, PhD, Lyncis UAB, Vilnius, Lithuania
3. Head of Sales, PhD, Lyncis UAB, Vilnius, Lithuania
Corresponding author: info@lyncis.org

Abstract

Currently the aluminium industry faces many challenges as it must deliver premium quality products for a competitive price while minimizing CO_2 emissions at the same time. Addressing these challenges is not possible without knowing the composition of raw and intermediate materials in the production process, ideally in real-time or near real-time. Traditionally prompt-gamma neutron activation analysis (PGNAA), X-ray fluorescence (XRF) and X-Ray diffraction (XRD) techniques have been used to get insight into mineral, chemical and elemental composition. The drawback with these techniques are harmful gamma, neutron, X-Ray radiation, high operational expenses, a need for frequent recalibration and limited analytical capabilities. This has lead to the emergence of the modern LIBS (Laser Induced Breakdown Spectroscopy) technology. Modern LIBS analyzers are completely safe, cost-effective, easy to maintain, and capable of analyzing both light and heavy elements. These instruments run 24/7/365 without additional recalibration and generate elemental composition data in real-time without any sample preparation directly on the conveyor belt or slurry pipes. With real-time data, it's possible to reject low-grade ore, blend different grades of bauxites, make real-time dosages of lime and sodium hydroxide, as well as to provide quality control of the final product. To ensure stable and accurate measurements in real-time, we use different chemometrics and machine learning optimization approaches. Traditional calibration methods provide rather poor results for real plant operation, where many other factors influence the results (i.e. variation in grain size and shape, density, moisture, material height on the conveyor belt and etc.). A range of comprehensive spectra filtration, normalization and advanced machine learning techniques were studied and implemented into our specialized software which provided good correlation with laboratory analysis data.

Keywords: LIBS, Online analysis, Bauxite, Alumina, Machine learning.

1. Introduction

Modern society is becoming more and more conscious of environmental protection and responsible companies strive to reduce waste streams, CO_2 emissions and energy consumption. Many of the efforts to *greenify* the production process require considerable investments and are hampered by the market demand for the supply premium quality products at a competitive price. Addressing these challenges is challenging without knowing the composition of raw and intermediate materials in the production process in real-time.

The chemical composition and mineralogy of bauxite ore vary from different mines or even different parts of the mine, open casts and storage. The presence of impurities such as silica, iron oxide and titanium in the bauxite ore, which is the main raw material used in the aluminium industry, not only influences its subsequent processing but also can increase production costs and compromise the quality of the final product, besides causing environmental pollution.

With real-time data, it is possible not only to reject low-grade ore, properly blend different grades of bauxites, but also to make real-time dosage of sodium hydroxide and lime and control the quality of the final product.

Growth in the global alumina supply and the tendency to extract lower grades of bauxite in the future will only increase the demand for reliable tools for real-time analysis that will provide the data required to control and remove impurities, make prompt corrections in the process without the need to wait several hours for lab results.

It is possible to solve these problems by sorting the raw materials by grades, including the rejection of the material unsuitable for a specific application, and by well-grounded adjustment of the processing parameters based on real-time information on the chemical composition of the material streams. This adjustment can be applied at all the production stages – from minerals survey, extraction, beneficiation and up to preparation of mixes with the pre-set composition and prompt automatic adjustment of the technological parameters.

In most cases, information on the chemical composition of materials on conveyers after extraction, crushing and blending that is required for the process control, averaging of stockpiles, batching of mixture components, becomes available to process operators only after several hours or the next day or after sampling. For large-tonnage production, such information delays significantly influence the impact of process control approaches. Besides, the precision of the information received is not always high enough, due to the complex procedures required to ensure the representativeness of the samples and their preparation for laboratory analysis.

2. Application of Online Analyzers for Alumina Production

The lack of uniform quality bauxite is an ongoing challenge for many alumina refineries. Bauxite ore consists of different minerals with silica, iron oxide and titanium as the major impurities. The proportion of the minerals varies depending on the bauxite source and sometimes within the same source.

Impurities contained in the bauxite are one of the major reasons for inefficiencies in the Bayer process. The caustic soda used in Bayer liquor is a critical raw material, having a significant influence on total operating costs in an alumina refinery. Its consumption largely depends on the composition of the bauxite that is used in the process and the chemistry of the desilication product as the result of digestion. The maximum concentration of silica in the final product is also strictly controlled due to its negative influence on the quality of the final product.

Online analyzers can provide a chemical composition and thus means for more accurate process control for process engineers in real-time (Figure 1).

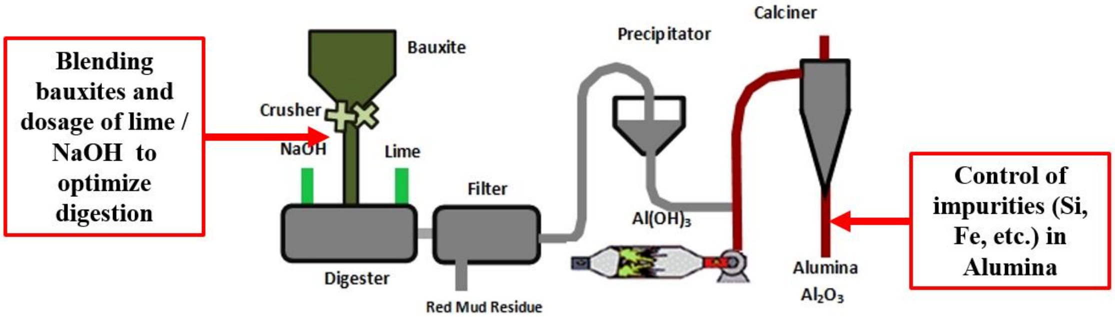


Figure 1. Possible points for online analysis.

Such tools make timely changes in the process possible. For example, this can help to remove impurities from the Bayer circuit (from bauxite ore or from liquor), control caustic soda consumption in desilication, scale formation (silica can cause problems with scale formation and quality of the final product). All this improves cost and energy efficiency, increases refinery output and reduces the variations in alumina quality.

Tools that can provide the chemical composition of the materials directly on conveyor belts or in slurry pipelines without sampling, and in real time, improve the efficiency of the operation [1–4]. However, most analyzers on the market are based on different sources of ionizing radiation (X-ray, neutron or gamma) which can be dangerous for the personnel and for the environment. Besides, such analyzers require special permissions from different state bodies dealing with radiation monitoring and are rather complicated from a technological point of view.

3. Industrial LIBS Analyzer

Lyncis LIBS analyzers have been demonstrated as a universal method to detect chemical and elemental composition in many industries since 2008. Without any sample collection and preparation directly on the conveyor belt or slurry pipe, it provides a chemical composition in real-time and allows the process engineers to make timely process adjustments. In contrast to other technologies, LIBS is completely safe, without any X-ray, neutron, or gamma radiation, and exceptionally easy and cost-effective to maintain. Lyncis LIBS analyzers are specially designed to withstand harsh industrial environment with high content of dust, moisture, corrosive salts, vibrations and temperature variation. In addition the influence of dust into bias of analysis results hasn’t been noticed.

LIBS analyzer uses solid-state pulsed Nd:YAG laser for excitation of the material being sampled. A laser beam with a pulse rate from 1 to 20 times per second is focused directly on the material on the conveyor belt or in the slurry pipeline, to heat a portion of the sample to temperatures around 30,000°C, which causes the sample to evaporate and transform into a plasma state. The plasma is a heavily ionized gas-like state of the material consisting of molecules, atoms, ions and electrons. The processes of recombination of positively and negatively charged particles begin in the plasma immediately and are accompanied by an emission of photons – «glow» of the plasma. The atom of every chemical element emits photons with strictly defined wavelengths with the intensity of light proportional to the concentration of this element in the sample. Therefore, the obtained spectra are specific to the analyzed material and are considered their «fingerprints» [5–7].

Optical emission of the plasma is collected with spectrometers within a wide range from 190 nm to 1000 nm and sent to a computer for analysis (Figure 2).

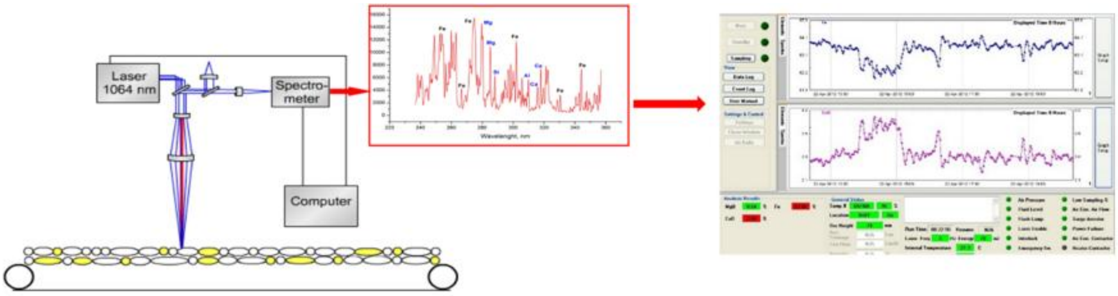


Figure 2. Principal scheme of an online LIBS system.

The spectra are processed statistically to provide concentrations of the elements present in the sample; this typically takes from 20 s to a few minutes [8].

LIBS analyzers are installed in the locations where material distribution is random (there is no systematic segregation). In most cases such locations can be easily identified in the process diagram. If random distribution is not available, a mixing can be arranged using simple and low cost devices like plows or chains. Accumulation and averaging of hundreds to thousands of spectra make the analytical results representative to full material flow on the conveyor belt.

The main advantages of the LIBS systems compared to other analytical methods typically used for elemental or chemical analyses are the following:

- high accuracy, low detection limits and high sensitivity due to clear spectral lines of most elements within a wide optical range with no interferences;
- simultaneous analysis of all light and heavy elements including Al, Si, Mg, C and etc.;
- completely safe without harmful ionizing radiation (X-ray, neutron, gamma)
- no need for permissions and regular inspections of the state bodies dealing with radiation monitoring;
- good accuracy regardless of particle size, changing height of the material on the conveyor belt and layer thickness;
- eliminated need for sample collection and preparation;
- stable long-term calibration;
- simple operation and maintenance;
- low cost of ownership.

Lyncis LIBS analyzers are being used in metallurgy, refractories, coal, lime, quartz, potash, phosphate fertilizer production [9–11]. Also, it has been tested on bauxite, alumina, non-ferrous metals ores, cement and other industrial materials. The analyzers are designed to operate 24/7/365 in automatic mode under extremely harsh industrial conditions (high humidity and temperature variation, vibration, high levels of dust). The analyzers can be integrated with any type of SCADA for automated sorting/crushing/dosage equipment control. According to user feedback, typical payback for Lyncis LIBS analyzers can be as low as a few months.

A breakdown of bauxite and alumina LIBS spectra is provided in Figure 3 and Figure 4. All major and minor elements and impurities: Al, Si, Fe, Mg, Ca can be identified and quantified with a high level of confidence.

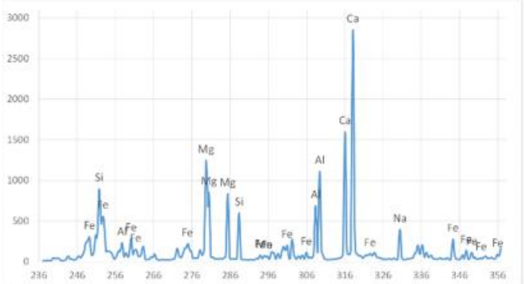


Figure 3. Typical bauxite UV spectrum.

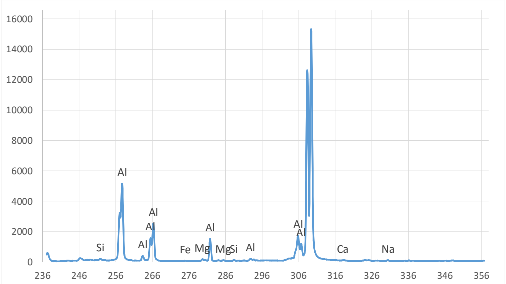


Figure 4. Typical alumina UV spectrum.

LIBS analytical lines are very clear with an excellent signal-to-background ratio which allows a very good correlation between online LIBS and traditional laboratory analysis results acquired using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Figure 5-6). Our experience over many years shows, that such a good correlation ensures successful industrial implementation.

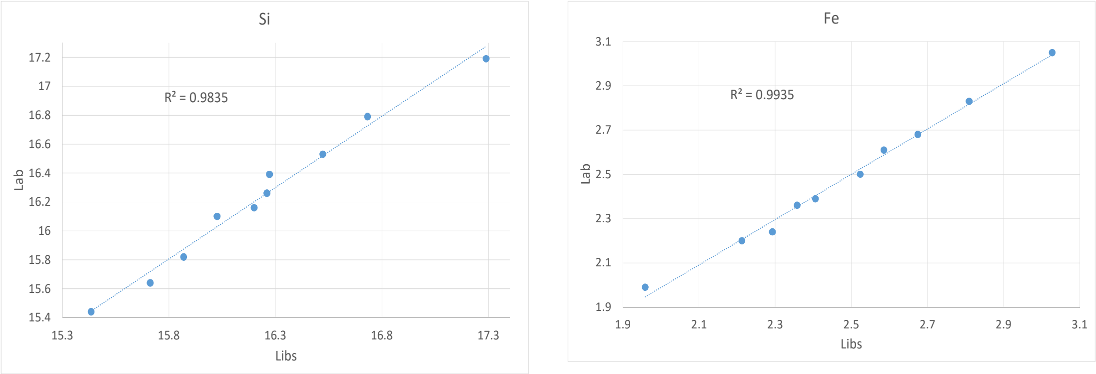


Figure 5. Comparison between online LIBS and laboratory data for bauxite samples (%).

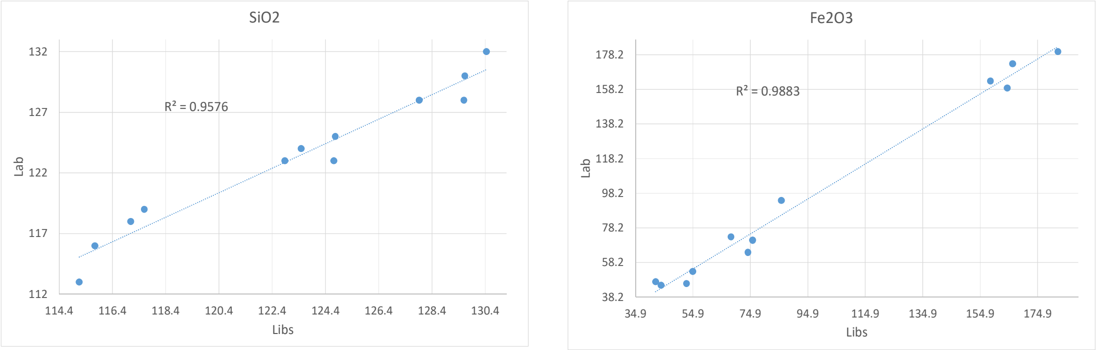


Figure 6. Comparison between online LIBS and laboratory data for alumina samples (ppm).

4. Advanced Analytical Approaches

To ensure stable accurate measurements in real-time, we use chemometrics and optimization approaches, as traditional calibration methods give rather poor results for real plant operation, where many other factors influence the results (e.g. weather conditions, variation in grain size, moisture level, etc.).

For a long time, specialists in the field of laser ablation and optical emission spectrometry (OES) have been working on solving the problem of calibration of LIBS systems. Even though Plasma Physics is a very complicated process, most mathematical models have long been based on the basic principles of analytical chemistry, where it is generally believed that the higher peak of the element under ideal laboratory conditions of the experiment is proportional to higher concentration of this element.

However, the need to analyze the material under industrial conditions, when, in contrast to the laboratory experiment, a large number of factors vary in addition to the actual concentration of the chemical elements studied, including the particle size distribution, material density, layer thickness on the conveyor belt, flow turbulence or laminarity in the case of liquid analysis, amount of dust, humidity and variations in ambient temperature at the measurement location, etc. all these factors lead to a number of challenges, which can't be solved by the classical approach described above.

These problems can be partly overcome using various types of calibration-free approaches, which can mitigate the impact of some of these factors. However, the accuracy of the tools calibrated according to these approaches makes it possible to perform only qualitative analysis of materials, usually within narrow concentration limits, and are therefore not always suitable for process control.

That is why Chemometrics, in which most of the methods are directly building on approaches widely used in Machine learning, have recently become very popular in LIBS and other techniques, offering a new perspective to this challenge.

The main stand-out feature of these approaches is the number of samples required for calibration. If 5–6 samples are enough to build a linear model based on peaks of 2–3 elements or a calibration-free model, the classic number of samples in data science is not even hundreds, but tens of thousands of samples, which is impossible in the conditions of industrial enterprises. The direct use of methods borrowed from Machine Learning leads to the illusion of building a good calibration on dozens of samples, which subsequently produces unreliable results in the real environment. For example, this can be observed as a result of the direct use of Artificial neural networks in LIBS and attempts to use Deep Learning only aggravate the problem [12].

Therefore, a key task in building a reliable calibration model with a limited number of samples is a proper integration of the Machine Learning methods into the general ideas about the physics of the process.

Below some methods that have proved themselves in practice are described. A lot of research in the field of LIBS uses the PCR (Principal Component Regression) method for calibration at the laboratory scale. At the industrial scale, PCA (Principal Component Analysis) can be used to pre-process data. The key advantage of this method is that it does not require tags (lab data) at all. Therefore, the training set can be formed not by the averaged spectra of the samples (there are few of them), but by the single spectra (it does not take long to get 10 000 spectra of the material, and the data volume already fully corresponds to the methods of Machine Learning). At the same time, it is possible to use a PCA decomposition not only for regression purposes (this usually does not allow achieving the required accuracy), but also for the purpose of data normalization. The issue is that with the PCA decomposition, the first one or two components describe not the required concentration fluctuations, but those undesirable effects mentioned above. Therefore, the following method is quite meaningful: obtaining a PCA decomposition for all available spectra, zeroing out the first 1–2 components in the diagonal matrix, and the subsequent inverse transformation. The spectra obtained at the output are fairly qualitatively differentiated in intensity and in the influence of moisture and non-focus. Since PCA is a technique of linear transformations, and many effects of plasma physics are fundamentally nonlinear, it also looks promising to replace PCA with Autoencoder, which, with a very similar ideology, uses more complex nonlinear models.

The second most important element in building models is the use of models of gradient descent with a learning rate not equal to 1. The selection of an effective learning rate largely depends on the volume of the training sample. The classical Machine Learning methods often involve very small values of the learning rate of the order of 10^{-6} or even smaller. However, this requires training sample sets of the classic volume for Machine learning. Therefore, to calibrate LIBS systems on several dozen samples, we can recommend the use of the learning rate in the range of 0.1–0.25. If several hundreds of samples are available, it is possible to consider values in the range of 0.03–0.1. The experience shows that a meaningful choice of the learning rate makes it possible to obtain much more stable formulas in the work, while also performing additional rationing of the spectra already in the calibration stage.

5. LIBS Software Solutions

The essential part of the methodology described above was implemented in the A.spect software – an analytical software developed by Lyncis for customers' needs and own use. The software allows the end user to perform a full range of operations required to build the ready-to-use calibration algorithms from the raw spectral data and chemical composition of the training data set.

To reduce the task dimension, the software performs a set of preliminary calculations on the spectra to determine the values of the most significant attributes for each peak (Figure 7). The attributes are calculated and averaged for each sample or exposition depending on user-defined parameters.

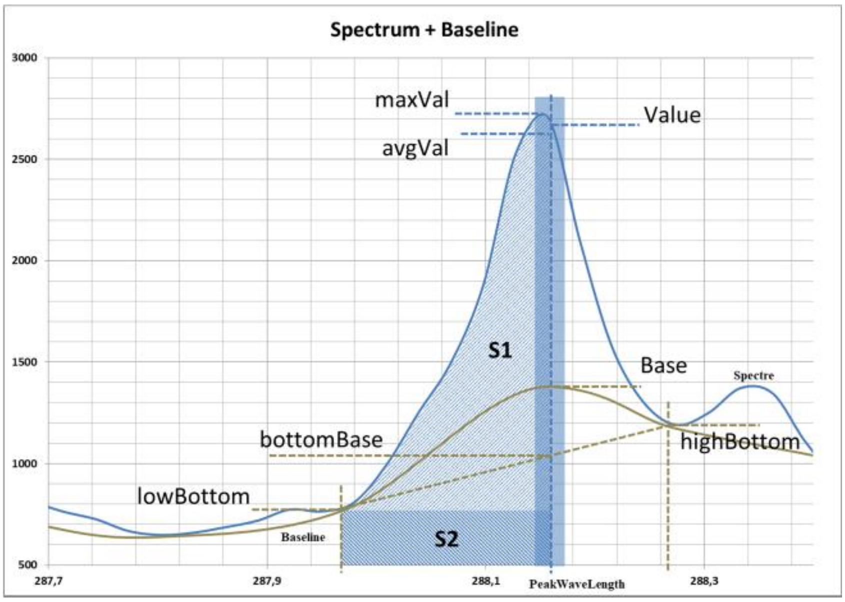
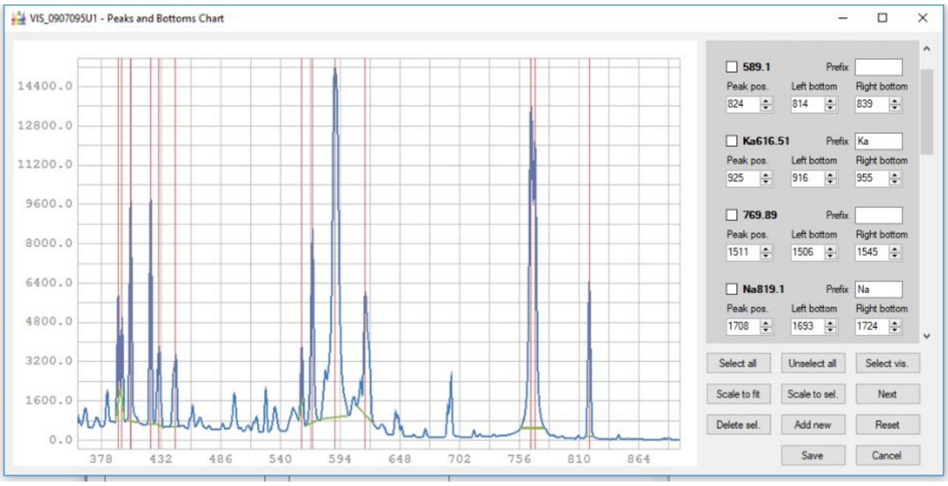


Figure 7. Key attributes of spectrum peaks.

The A.spect application allows the user to perform spectra markup, i.e. to predefine positions of peaks and bottoms, automatically or manually. Automatic markup is based on the spectrum averaged for the entire training set. The option of manual markup change is useful to define the valuable peaks, which may be omitted on such an average spectrum.



☐ **589.1** Prefix

Peak pos.	Left bottom	Right bottom
824	814	839

☐ **Ka616.51** Prefix Ka

Peak pos.	Left bottom	Right bottom
925	916	955

☐ **769.89** Prefix

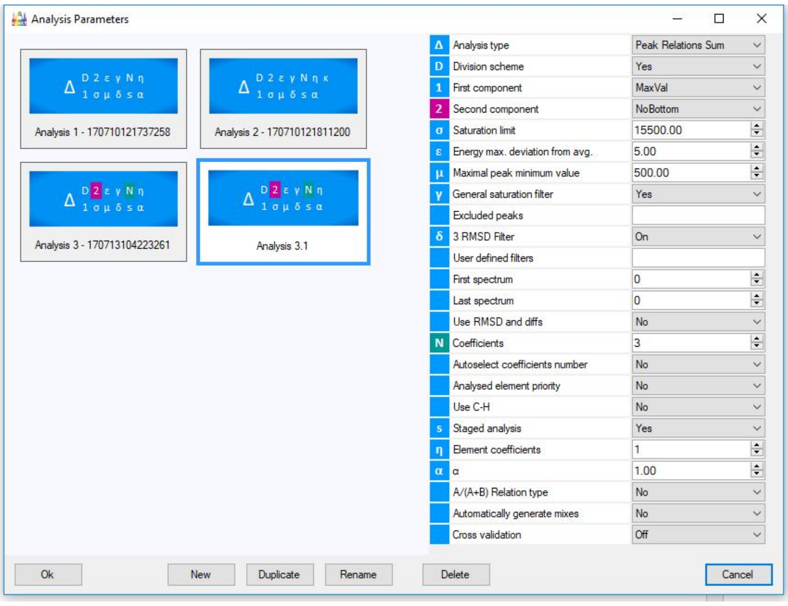
Peak pos.	Left bottom	Right bottom
1511	1506	1545

☐ **Na819.1** Prefix Na

Peak pos.	Left bottom	Right bottom
1708	1693	1724

Figure 8. Spectra mark-up.

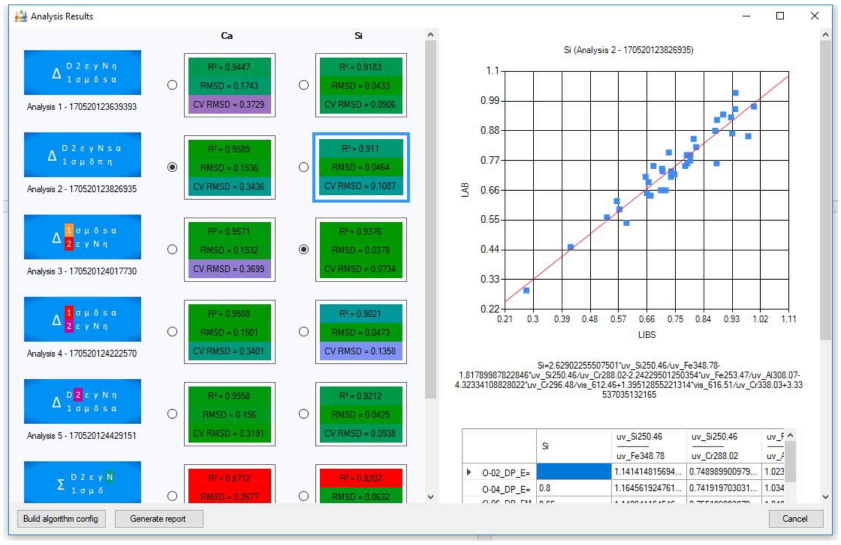
The A.spect application also supports different types of calibration algorithms and formulas, including the option of a user-defined formula. The set of parameters depend on the selected analysis type.



Δ	Analysis type	Peak Relations Sum
D	Division scheme	Yes
1	First component	MaxVal
2	Second component	NoBottom
σ	Saturation limit	15500.00
ε	Energy max. deviation from avg.	5.00
μ	Maximal peak minimum value	500.00
γ	General saturation filter	Yes
	Excluded peaks	
δ	3 RMSD Filter	On
	User defined filters	
	First spectrum	0
	Last spectrum	0
	Use RMSD and diffs	No
N	Coefficients	3
	Autoselect coefficients number	No
	Analysed element priority	No
	Use C-H	No
s	Staged analysis	Yes
η	Element coefficients	1
α	α	1.00
	A/(A+B) Relation type	No
	Automatically generate mixes	No
	Cross validation	Off

Figure 9. Analysis parameters.

Variations in parameters and the ability to run several calculations at once allow researchers to be flexible in comparing the main spectral properties of the material and their relationship with its chemical and, in some cases, mineralogical composition and obtain the best calibration algorithms.



		Ca		Si
Δ D 2 ε γ N η 1 σ μ δ s α Analysis 1 - 170520123639393	○	R² = 0.9447 RMSD = 0.1743 CV RMSD = 0.3729	○	R² = 0.9183 RMSD = 0.0433 CV RMSD = 0.0906
Δ D 2 ε γ N s α 1 σ μ δ π η Analysis 2 - 170520123826935	●	R² = 0.9589 RMSD = 0.1536 CV RMSD = 0.3436	○	R² = 0.911 RMSD = 0.0464 CV RMSD = 0.1087
Δ 1 σ μ δ s α 2 ε γ N η Analysis 3 - 170520124017730	○	R² = 0.9571 RMSD = 0.1532 CV RMSD = 0.3699	●	R² = 0.9376 RMSD = 0.0378 CV RMSD = 0.0734
Δ 1 σ μ δ s α 2 ε γ N η Analysis 4 - 170520124222570	○	R² = 0.9588 RMSD = 0.1501 CV RMSD = 0.3401	○	R² = 0.9021 RMSD = 0.0473 CV RMSD = 0.1358
Δ D 2 ε γ N η 1 σ μ δ s α Analysis 5 - 170520124429151	○	R² = 0.9558 RMSD = 0.156 CV RMSD = 0.3191	○	R² = 0.9212 RMSD = 0.0425 CV RMSD = 0.0938
Σ D 2 ε γ N 1 σ μ δ	○	R² = 0.8712 RMSD = 0.2677	○	R² = 0.8202 RMSD = 0.0632

Si=2.62902255507501*uv_Si250.46/uv_Fe348.78-1.81789987822846*uv_Si250.46/uv_Cr288.02-2.24229501250354*uv_Fe253.47/uv_Al308.07-4.32334108828022*uv_Cr296.48/vis_612.46+1.39512855221314*vis_616.51/uv_Cr338.03+3.33537035132165

	Si	uv_Si250.46 / uv_Fe348.78	uv_Si250.46 / uv_Cr288.02	uv_F / uv_A
O-02_DP_E=		1.141414815694...	0.748989900979...	1.023
O-04_DP_E=	0.8	1.164561924761...	0.741919703031...	1.034

Figure 10. Analysis results.

The algorithms and their optimal default parameters, developed at the stage of studying the spectral properties of the material and performing the on-site calibration of the analyzer, allow even beginner-level users (technicians and laboratory staff) to achieve good results not only at the initial on-site calibration but also in its further adjustment, as more data on the properties of the material on the conveyor belt will be accumulated, which cannot be studied during the initial commissioning period and vary depending on the material supply with different chemical and mineralogical compositions, variations in density, particle size distribution, moisture and temperature.

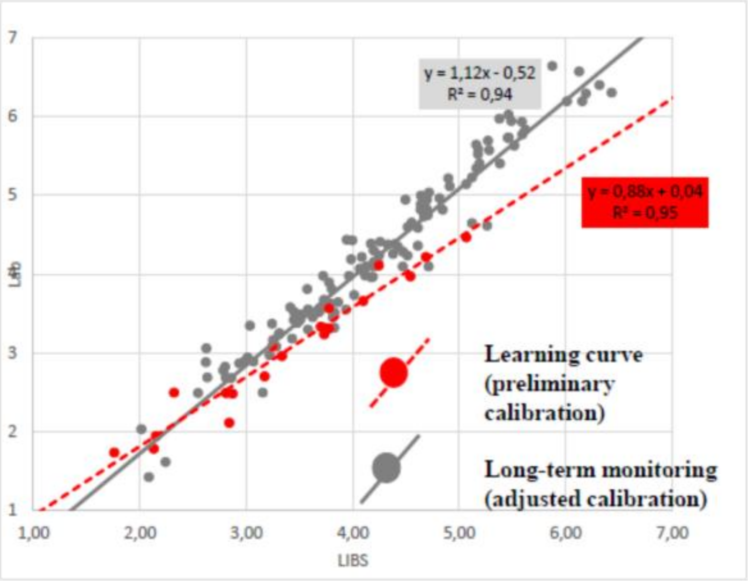


Figure 11. Long-term calibration.

Our experience shows that in order to get a stable algorithm that can work for a long period, the user of the system needs to carefully monitor the readings of the analyzer for several months after the commissioning and, if necessary, add new calibration samples to the calibration algorithm to take into account the factors described (Figure 11).

6. Conclusions

It has been demonstrated that LIBS analyzer technology is well suited for the online analysis of bauxite and alumina without any sample preparation for real time process control. Both major and minor elements and impurities – Al, Si, Fe, Mg, Ca can be identified and quantified with a high level of confidence. Safety, low cost maintenance and excellent analytical performance of LIBS analyzers make it advantageous against traditional techniques like PGNAA, XRF or XRD. Further installation of online analyzer for real time control of blending of bauxite ore, lime dosage or quality control of final product should follow.

7. References

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