

Experience in applying online elemental analysis to steel- and ironmaking

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Summary

Operation managers are constantly assessing the productivity of their processes. Variations in mineralogy and the presence of impurities, not only influence on the effectiveness of the processes, but also increase production costs. Online chemical analysis of material flows directly on site is critical for timeous interventions to improve process performance and eliminate the need for laboratory analysis, often involving hours of delay and potential human error. Lyncis, using knowledge and experience accumulated in the industrial applications, offers the solution for stable accurate online measurements under production conditions, where many factors such as mineralogy, grain size, moisture, etc., influence results. Our analyzers use a fully safe laser optical emission technology without hazardous radiation, provide long-term stable calibration, easy and low-cost maintenance. Online technology allows to detect all elements of interest in real-time, directly on site, without sampling, on conveyor belts and in slurry pipelines, eliminating the need for continuous laboratory analysis, often involving hours of delay, and potential human error. The laser induced breakdown spectroscopy technology we are using in online analysis do not produce any ionizing radiation. The analyzers operate 24/7/365 in automatic mode in severe industrial conditions for many years in metals, fertilizer, refractories and industrial minerals applications. The wide range of chemometric and optimization techniques are used to ensure stable accurate measurements in real time mode.

Key Words

LIBS, online analysis, ironmaking, steelmaking, sintering, pelletizing, refractories.

Introduction

Variations in mineralogical composition and influence of such impurities as silica, calcium, aluminum and magnesium in iron ores, not only affect processing efficiency, but can also increase production costs and create quality deficits in the final product. Real-time chemical analysis allows operation managers to control ore grades, reject unacceptable material, blend different grades, adjust the necessary amount of fluxes, coal, coke and other process raw materials in real-time and to improve product quality control.

The increasing volumes of global iron and steel supply and the necessity to process lower grades of iron ore in future will only intensify the demand in reliable tools for real-time quality control. The online measurements can provide the data required for managing impurities and prompt adjustment of the process parameters without the potential delays of up to several hours for sampling and laboratory based results. For large-tonnage production, such delays significantly influence the efficiency of the process control. Therefore, it is very useful to understand any real-time variation in the quality of the feed for processes where settings must assume obtaining raw materials with stable predetermined quality parameters.

Problems arising from quality variations can be solved by sorting raw materials by grade, rejecting of the material unsuitable for certain applications and by timely adjustment of the processing parameters based on the real-time measurement. This information can be used to control the technological process at all production stages, from minerals survey, mining, beneficiation and up to the preparation of feed grades with more precise predefined composition and prompt automatic adjustment of the processing settings.

1. Application of Online Measurement Tools in Iron and Steel Production

Many iron and steel factories suffer from the loss of efficiency due to the lack of uniform iron ore quality. Iron ore consists of various minerals, where major impurities are silica, aluminum, magnesium, calcium. The actual mineralogical composition varies depending on the iron ore source and production grades from the same source. The variation of impurities in iron ore and unstable basicity of sinter are major causes of the inefficiency in the blast smelting process due to high coke consumption and slag properties fluctuations.

For example, the MAYA online elemental analyzer based on LIBS (Laser Induced Breakdown Spectroscopy) is used at NLMK (Novolipetsk Steel) to stabilize the composition of the raw material mix. The information about content of Fe, Ca, Si, Mg etc. has a crucial importance in the sinter production since the iron ore chemical composition varies considerably. The bad averaging and segregation of the materials in pile is one of the reasons

of such variations. Adding lime into the iron-ore pile for moisture fixation has a major impact on variations. This is one of the major problems to obtain the sinter with the stable content of Fe and basicity factor (CaO/SiO_2). The quality of the iron-ore materials (sinter and pellet) has a significant influence on efficiency of blast furnaces operation. The reduction of the sinter basicity variation leads to reducing of the output of slag per ton of cast iron and to decreasing of the coke rate in blast furnaces.

The MAYA online laser analyzer installed on the conveyor of agglomeration burden coming to the sinter machine before flux batching provides information about content of Fe, CaO and SiO_2 in the iron-ore mixture to the control system that performs the continuous automatic control of the flux flow rate at subsequent batching, decreasing the agglomeration basicity variations. The harsh condition in “Novolipetsk Steel” with high dust level, vibrations and temperature variations from $-10\text{ }^\circ\text{C}$ to $+40\text{ }^\circ\text{C}$ significantly complicated the task. However, the analyzer successful has been successfully operating round-the-clock without failures since 2011.

After the installation of the MAYA at NLMK, the portion of agglomerate, which basicity deviated from the value specified by the blast furnace shop by more than 0.05 was decreased by more than twice – from 8-10 % down to 3-4 %. The saving of flux in the blast furnace shop was reduced by more than 0.6-0.8 kg per ton of cast iron. The period of cost recovery for the project was equal to less than 6 months.

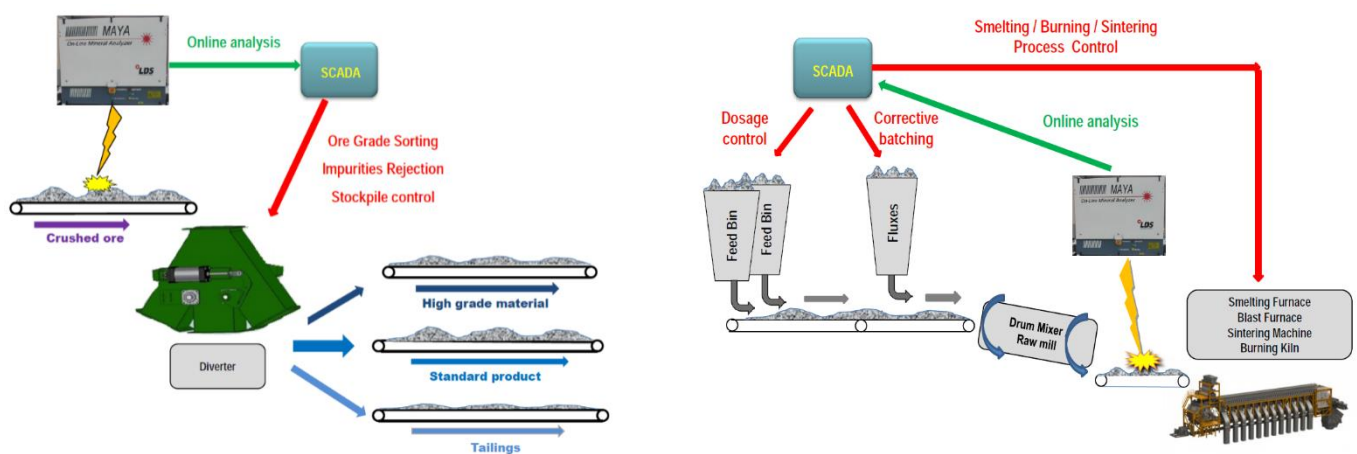


Figure 1. Possible locations for online measurement.

Tools that can provide real-time information on chemical composition of the materials directly on conveyor belts or in slurry pipelines without sampling improve the efficiency of the operation and increase the correspondence of analytical information to real composition of the material flow [1 - 4]. However, most analyzers on the market are based on different sources of ionizing radiation (X-ray, neutron or gamma), presenting risks to operating personnel and the environment. Such analyzers usually require special certification from regulatory bodies dealing with radiation monitoring, and are often complicated pieces of technology.

2. Industrial LIBS Analyzer

Lyncis offers laser analyzers detecting all elements of interest in real-time, without sampling, directly on site, on conveyor belts and in slurry pipelines, eliminating the need for continuous laboratory analysis which often involves hours of delay from the sampling time, and subject to potential human errors. The analyzers are based on Laser Induced Breakdown Spectroscopy (LIBS) and do not produce any ionizing radiation. The wide experience accumulated in the manufacture, calibration and maintenance of the online LIBS analyzers is successfully used by the Lyncis team to bring the LIBS analyzers to a new level.

The operating principle of Lyncis analyzers is laser induced breakdown spectroscopy, where the solid-state pulsed laser serves as an excitation source for the material studied. With a measuring rate from 1 to 20 times per second, the laser beam is focused on the surface of the material being analyzed and a small sample of the substance is excited into a plasma state. The plasma is practically electrically neutral, but heavily ionized gas containing the molecules, atoms and ions of the chemical elements of the material being measured, in addition to free electrons. The processes of recombination of positively and negatively charged particles begin in the plasma immediately and are accompanied by emission of photons, producing the plasma “glow”. The atoms of every chemical element emit photons with strictly defined wavelengths, and the emission intensity is proportional to the concentration of this element in the material analyzed. The spectra measured characterize the analyzed material [5-7].

The optical radiation of the plasma within wide optical range from 190 to 1000 nm is measured with special spectrometers before transferring the digital information of the spectral composition to the computer in the analyzer (see Figure 2).

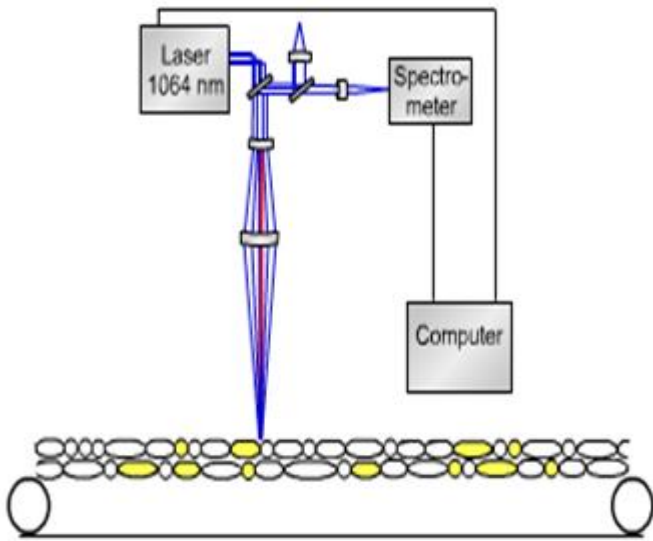


Figure 2. Principal scheme of a LIBS system.

As a result of the statistical processing of a spectra set for the period of time required to resolve the production measurement (usually from 20s up to several minutes), the concentrations of the elemental components of the material analyzed are calculated.

The main advantages of the LIBS systems compared to the other analytical methods 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;
- the ability to analyze simultaneously all elements of interest, including light elements (Si, Mg, Al, C,);
- no ionizing radiation (neutron, gamma and X-ray) risk for production personnel, no requirement for special permits or regular inspections by the regulatory bodies dealing with radiation monitoring;
- good accuracy regardless of bulk size, surface quality, thickness of the material layer on the belt;
- stable long-term calibration;
- simple and safe operation and maintenance;
- low-cost ownership.

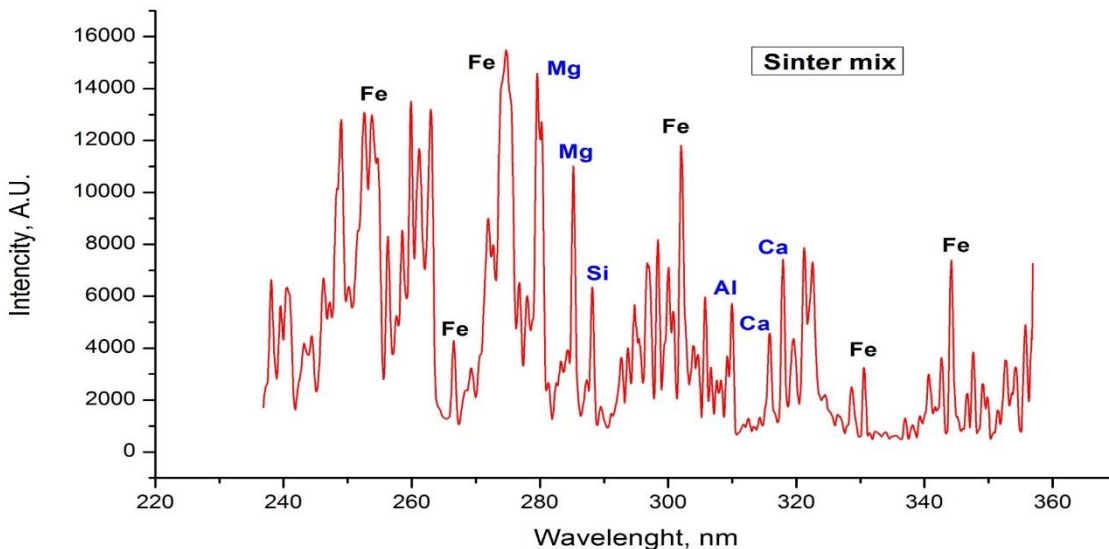


Figure 3. Typical sinter mix UV spectrum.

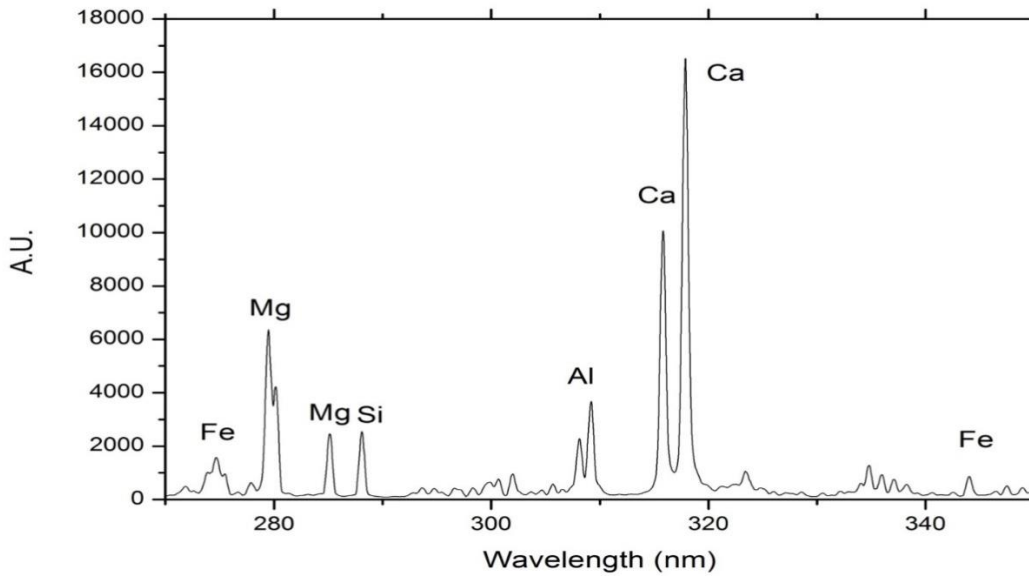
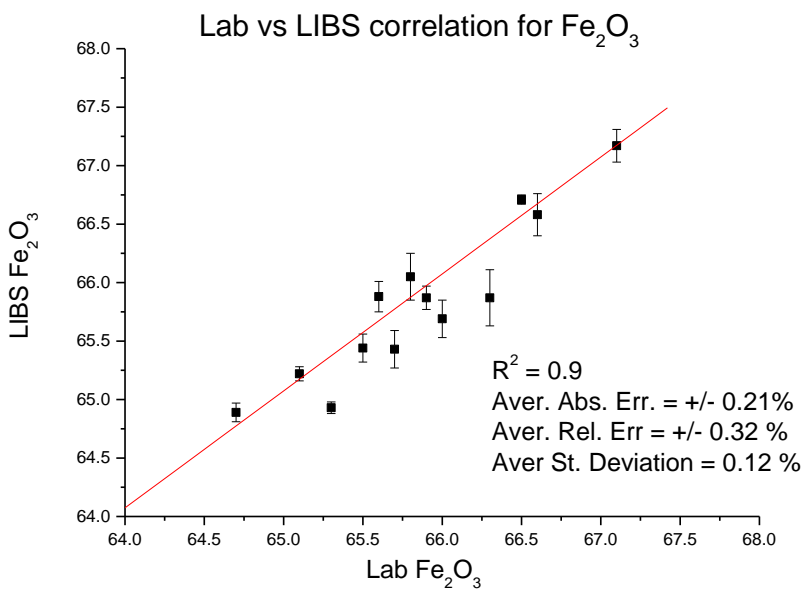


Figure 4. Typical limestone UV spectrum.

Our analyzers are currently used in the steel, refractory, potash and phosphate industries [9-11]. It has also been successfully tested in coal, non-ferrous and cement industries and in the production of various industrial materials (lime, limestone, quartz, etc.). The analyzers were designed to operate in automatic mode 24/7 under very harsh industrial conditions (high humidity and temperature variation, vibration, dustiness, etc.). They can be easily integrated with any customers' SCADA and sorting/crushing/dosage equipment for process control. According to our customers' feedback, a typical payback period for our system is only several months.

Figures 3 and 4 present breakdown spectra of sinter mix and limestone. Both major, Fe, and minor elements, impurities, such as Si, Mg, Ca, Al, C can be confidently identified, measured and used for calculation of such important parameters as basicity and loss on ignition that is the sum of contributions from the mass loss of volatile compounds water vapour, carbon dioxide and sulfides and the mass gain due to oxidation (Fe II to Fe₂O₃). The determination of LOI is essential in sinter plant and blast furnace balance calculations, as it is used to calculate calcinated elemental concentrations.

Clear analytical lines enable very good correlation between online LIBS and traditional laboratory results (Figure 5). According to our accumulated experience, such data indicates successful industrial implementation.



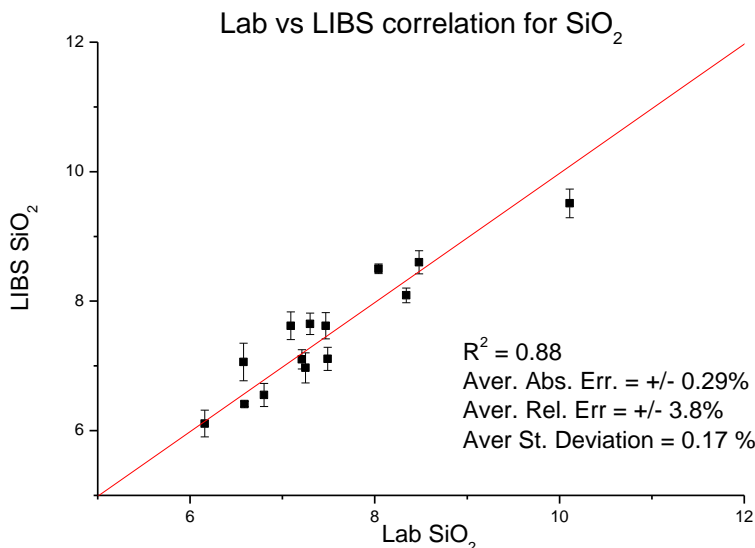
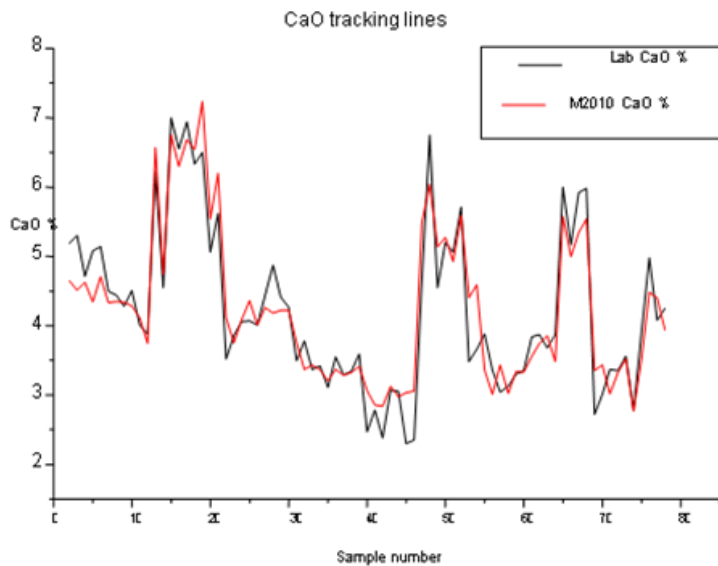


Figure 5. Comparison between online LIBS and laboratory data for sinter mix samples.

3. Advanced Analytical Approaches

For a long time, specialists in the field of laser ablation and optical emission spectrometry (OES) have been solving the problem of calibration of LIBS systems. Despite the fact that Plasma Physics is a very complicated field, most mathematical models have long been based on the basic principles of analytical chemistry, where it is generally believed that the growth of the peak of the element under ideal laboratory conditions is proportional to the increase in the concentration of this element. However, the need to analyze materials under industrial conditions, where, in contrast to the laboratory environment, a large number of factors vary in addition to the actual concentrations of the elements studied, including particle size distribution, material density, layer thickness on the conveyor belt, flow turbulence or laminarity in the case of liquid analysis, dustiness, humidity, variations in ambient temperature at the measurement place, etc. All these factors lead to a number of challenges, which cannot be solved by the classical approach.

These challenges can be partly overcome and their impact mitigated using various types of calibration-free approach. However, the accuracy of the tools calibrated by this approach only allow qualitative analysis of materials, and are not always suitably accurate or precise for process control, often expected to be within narrow concentration limits. That is why chemometrics, in which most of the methods are directly borrowed from those widely used in machine learning, has become recently very popular in LIBS, providing a new approach to task solving from a machine learning perspective.

The main 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. This is absolutely impossible under the operating 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 a 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. Therefore, the key challenge in building a reliable calibration with a limited number of samples is the proper integration of machine learning methods into the general ideas about the physics of the process.

Some methods that have proved themselves in practice are described below. Many works in the field of LIBS use 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).

The second most important element in building models is the use of models of gradient descent with learning rate not equal to 1. Selection of an effective learning rate largely depends on the volume of the training sample. The classic Machine Learning often involve very small values of the learning rate of the order of 10^{-6} and 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 at the level of 0.1 - 0.25, if several hundreds of samples are available, it is possible to consider the values about 0.03 - 0.1. The experience shows that a meaningful choice of the learning rate makes it possible to obtain much more stable formulas, while also performing additional rationing of the spectra already at the calibration stage.

The essential part of the methodology described above was implemented in the analytical software developed by Lyncis for their 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 algorithm from the raw spectral data and chemical composition for the training set. To reduce the task dimension, the software performs a set of preliminary calculations for spectra to determine the values of the most significant attributes for each peak. The attributes are calculated and averaged for each sample or exposition depending on user-defined parameters. Variations in parameters and the ability to run several researches at once allow user to be flexible in comparison of 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.

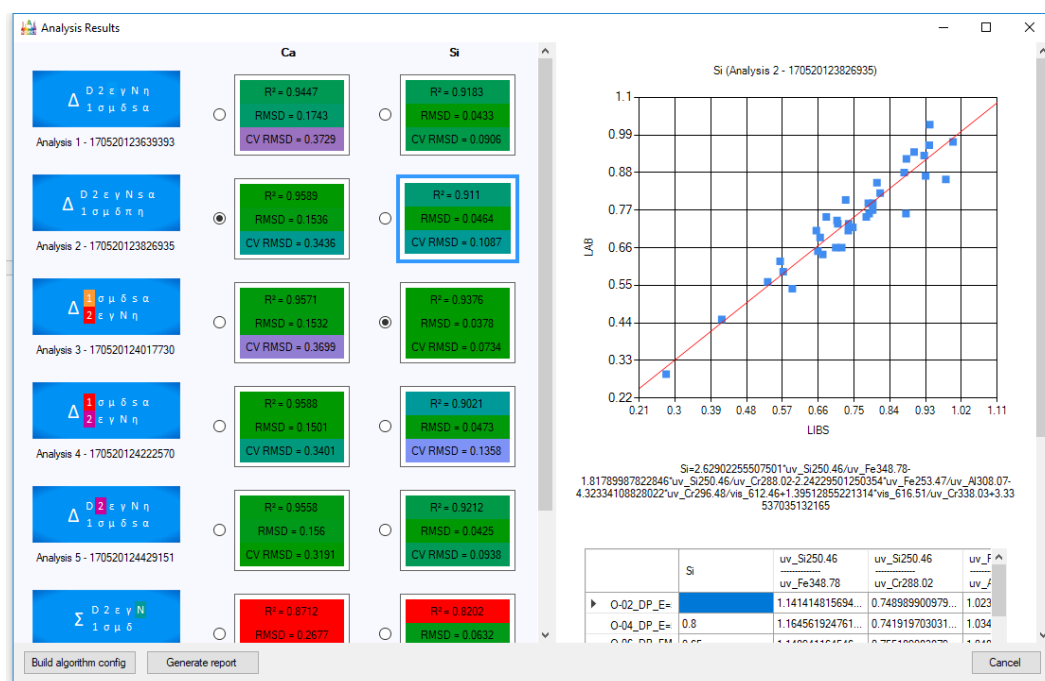


Figure 6. Analysis results in Lyncis's analytical software.

The algorithms and their optimal default parameters, developed at the stage of studying the spectral properties of the material and performing of the on-site calibration of the analyzer, allow even the 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. This is required as more data on the properties of the material on the conveyor belt are 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.

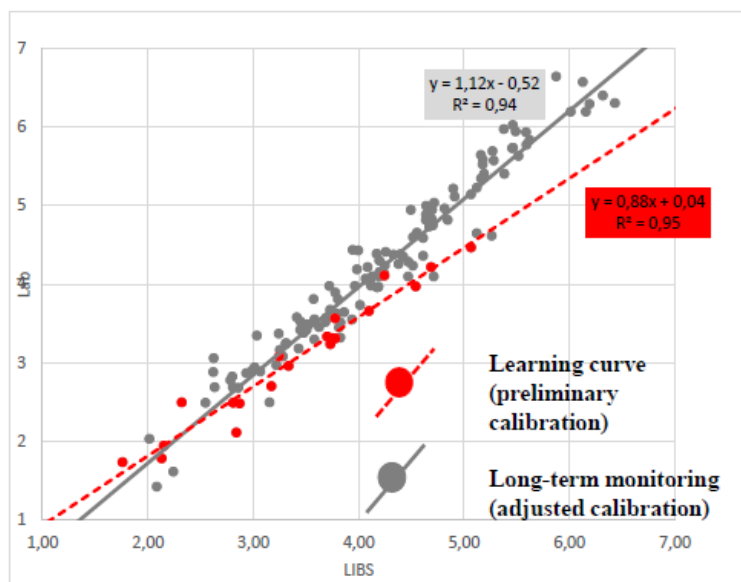


Figure 7. Long-term calibration.

Our experience shows that to get a stable algorithm that can work for a long period, the system user needs to carefully monitor the analyzer readings for several months after commissioning and, if necessary, add new calibration samples to the calibration algorithm to take into account the factors described (see Figure 7).

Conclusion

Online elemental analyzers play significant role in the digital transformation of the steel- and ironmaking, providing operation managers with automatic continuous quality control and timeous decision support. Real-time measurement of elements of interest and necessary impurities allows more flexible and efficient use of available raw materials, ensures stable composition of furnace feed, especially for basicity and Carbon content, as well as gives possibility to control necessary amount of fluxes. MAYA online elemental analyzers brings together experience in the industrial installations and advance analytics to enable timely, safe (no ionizing radiation) and accurate decision making at every stage of the process. LYNCS uses various chemometric and optimization techniques to ensure long-term stable operation and accurate online measurement on the site.

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