

# LASER-INDUCED BREAKDOWN SPECTROSCOPY: A STEP CLOSER TO ON-LINE QUALITY CONTROL OF SLAGS?

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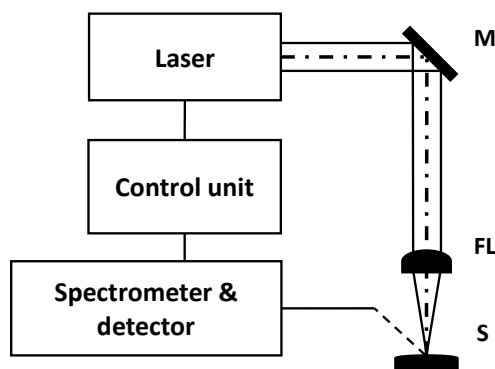
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## Introduction

Laser-induced breakdown spectroscopy (LIBS) is an analytical tool to determine the elemental composition of materials. The technique is based on a plasma induced by a pulsed laser; commonly Nd:YAG lasers are employed. The laser pulse is focused on the sample surface using mirrors and focusing lenses (Figure 1). The sample heats up locally and starts boiling and evaporating, generating a plasma. Its irradiation is resolved spectrally, resulting in a fingerprint of the material's elemental composition.



**Figure 1:** Systematic drawing of a LIBS setup; M: mirror; FL: focus lens; S: sample

LIBS is interesting for on-line compositional analysis of pyrometallurgical process streams, which are conventionally measured off-site using XRF or spark-discharge OES. Advantages of LIBS for on-line analysis over aforementioned techniques are: independence of the material's state, remote analysis, no sample preparation required and the resulting decrease in analysis time. One of the investigated LIBS applications is slag analysis, mainly from steel industry<sup>1,2</sup>. Since the composition of slag varies significantly from batch to batch, one of the major challenges for slag analysis is the matrix effect. It occurs when large varieties are present in the chemical composition of the targets<sup>1</sup>. As a result, conventional calibration methods, such as univariate linear regression, are often inadequate, causing dubious results. In order to improve quantitative performance, multivariate calibration methods are used, such as partial least squares (PLS)<sup>3</sup>. These methods exhaust the correlation between the obtained spectrum and the reference values to reveal underlying patterns<sup>3</sup>, whereas univariate calibration solely takes into account selected emission lines.

In this paper, LIBS is presented as a potential technique for the analysis of non-ferrous slags. A first analysis was performed on solid synthetic slags, with compositions ranging in the fayalite region ( $\text{Fe}_2\text{SiO}_4$ ) in order to calibrate the system and determine the accuracy and limits of detection (LOD). Both univariate and multivariate calibration methods were used and compared.

## Materials and Methods

Ten slag samples, based on the fayalite slag system, were synthesised on lab-scale. Chemical powders (purities > 96%) were mixed and individually melted in a Therm-Aix vertical tube furnace using an Fe crucible at a temperature above 1200°C to obtain a fully liquid melt. During synthesis, an inert atmosphere was maintained by flushing Ar gas. After one hour at maximum temperature, the samples were quenched in water to obtain an amorphous structure upon solidification. Afterwards, the slag samples were dried at 80°C. The dried slag was imbedded in hardening resin, grinded and polished using 1  $\mu\text{m}$  diamond paste. The polished sections were used for electron micro-probe analysis (JEOL JXA-8530F, 15 kV and 30 nA). Table 1 lists the normalised compositions measured using EPMA-WDS. Samples 1-5 were designed to range in concentrations of  $\text{SiO}_2$  and  $\text{CuO}$  with constant  $\text{Al}_2\text{O}_3/\text{FeO}$  ratio (0.069), whereas samples 6-10 to range in concentrations of  $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$  with constant  $\text{SiO}_2/\text{FeO}$  ratio (0.45). The  $\text{CuO}$  concentration was aimed to range from 0.1 to 1.0 wt%. However, the EPMA analysis revealed that the  $\text{CuO}$  was not fully incorporated in the slag during synthesis, resulting in lower than expected values.

**Table 1:** Normalised composition of synthetic slag measured using EPMA-WDS (wt%)

Slag n°	1	2	3	4	5	6	7	8	9	10
$\text{SiO}_2$	21.7	24.8	27.8	31.3	36.3	28.3	27.6	27.8	28.2	28.3
$\text{Al}_2\text{O}_3$	5.2	4.7	4.5	4.3	4.0	8.2	6.4	4.4	2.3	0.0
$\text{FeO}$	71.8	69.5	64.8	63.4	58.8	60.9	62	62.1	62.4	62.9
$\text{ZnO}$	-	-	-	-	-	1.6	3.0	4.7	6.0	7.6
$\text{CuO}$	0.1	0.1	0.2	0.1	0.1	-	-	-	-	-
$\text{SnO}_2$	1.2	1.0	1.1	0.9	0.8	1.1	1.1	1.1	1.1	1.2

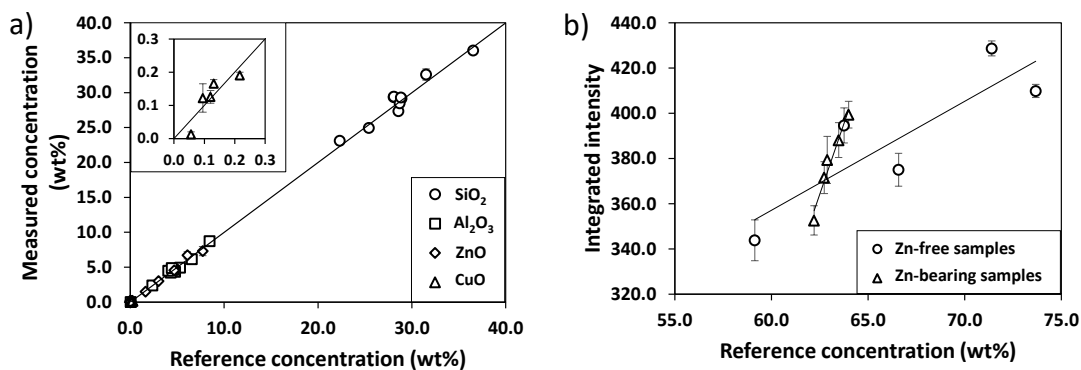
LIBS analysis was performed on polished sections at ERCo<sup>4</sup> (Plainfield, NJ, USA). A pulsed Nd:YAG laser (1064 nm, 330 mJ/pulse) was used to induce plasmas on the sample surface. Five spectra were collected per sample using an Echelle-type spectrometer, each spectrum consisting of the average irradiation of 100 plasmas. Recorded spectra were processed using software packages Excel 2013, Eclipse and JMP pro 13. For the univariate calibration, emission lines were selected for each element of interest and the area below these lines was calculated using the trapezium rule. The integrated intensities were normalised using local background values. Based on the calibrations, the %accuracy error, which explains the deviation of the measured value from the reference value, was calculated<sup>2</sup>. LODs were defined as  $3 \cdot \text{NC}/I$  with  $N$  the noise calculated as the standard deviation of the local background around the

emission line,  $C$  the lowest concentration found in the standard samples and  $I$  its maximum intensity measured at the corresponding emission line<sup>2</sup>.

## Results and Discussion

### Univariate Calibration

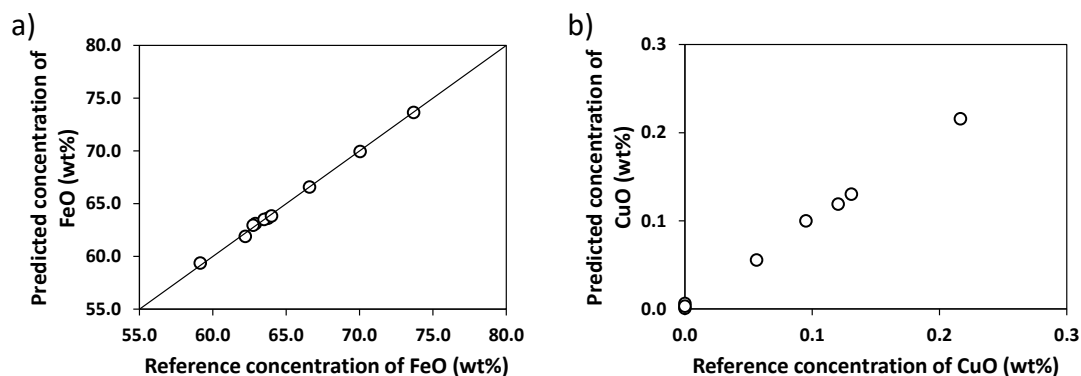
Figure 2a shows the measured concentrations using LIBS versus the reference concentrations from EPMA-WDS for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZnO}$  and  $\text{CuO}$ . Using linear regression, good correlations are obtained for  $\text{Al}_2\text{O}_3$  ( $R^2 = 0.9784$ ) and  $\text{ZnO}$  ( $R^2 = 0.9903$ ). In case of  $\text{SiO}_2$  a lower  $R^2$  value of 0.8966 was observed. However, when using second order regression, as was done by Vrenegor *et al.*<sup>5</sup>, the  $R^2$ -value of  $\text{SiO}_2$  is improved to 0.9604. With the applied LIBS parameters, the signal of Si saturates at higher concentrations, resulting in lower intensities. The correlation of  $\text{CuO}$  content with the LIBS signal is poorer ( $R^2 = 0.7558$ ). Figure 2b shows the FeO content versus the observed LIBS signal. Two trends are visible; a steep regression line which is characterised by samples containing ZnO in the matrix (triangles,  $R^2 = 0.9559$ ), whereas the other samples (circles,  $R^2 = 0.7424$ ) are more scattered.



**Figure 2:** a) measured concentrations of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZnO}$  and  $\text{CuO}$  (upper left corner) using LIBS vs. the reference concentrations from EPMA-WDS, b) Univariate calibration of FeO

### Multivariate Calibration

Figure 3 shows the concentrations calculated from LIBS using PLS regression for FeO and  $\text{CuO}$  to the reference concentration measured with EPMA-WDS. A considerably better correlation ( $R^2 = 0.9983$ ) is obtained for FeO (Figure 3a) in comparison with univariate calibration. The same can be observed for  $\text{CuO}$  where an  $R^2$ -value of 0.9876 is achieved, representing an improved regression (Figure 3b). The  $R^2$ -values of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$  are 0.9862, 0.9896 and 0.9954, respectively, which are similar to the results obtained using univariate calibration. Table 2 lists the %accuracy errors and LODs obtained for the different calibration methods used.



**Figure 3:** Partial least squares regression for a) FeO and b) for CuO

**Table 2:** Accuracy error (in %) and LOD (in ppm) of the elements of interest (UV = univariate, UV2 = second order univariate, MV = multivariate calibration)

	SiO <sub>2</sub>			Al <sub>2</sub> O <sub>3</sub>		CuO		ZnO		FeO	
Regression	UV	UV2	MV	UV	MV	UV	MV	UV	MV	UV	MV
Accuracy error (%)	3.9	2.6	1.2	5.9	3.1	27.5	1.6	5.2	4.0	5.7	0.2
LOD (ppm)	-			2200		26		3100		-	

## Conclusions

In this paper, LIBS is presented as a promising analytical tool for non-ferrous slag analysis. Calibration results are shown using solid synthetic slag samples and good correlations were obtained for the investigated elements by using univariate regression in case of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and ZnO and multivariate regression models in case of FeO and CuO. Focus of future work will be on molten fayalite slag systems in order to evaluate the potential industrial implementation.

## References

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