



Technical Note

Analysis of slags using laser-induced breakdown spectroscopy☆



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ABSTRACT

The feasibility of laser-induced breakdown spectroscopy (LIBS) for the analysis of gasification slags was investigated by comparing LIBS results to the results of an ICP-OES analyzer. A small amount of slag sample was placed on a piece of double sided adhesive tape attached to a glass microscope slide and analyzed for Al, Ca, Fe, Si, and V which are major elements found in slags. The partial least squares regression (PLS-R) and univariate simple linear regression (SLR) calibration methods indicated that apart from V (accuracy up to +20%) the accuracy of analysis varies within 0.35–6.5% for SLR and 0.06–10% for PLS-R. A paired-sample t-test within the 95% confidence level yielded p-values greater than 0.05, meaning no appreciable statistical difference was observed between the univariate SLR with internal standardization and the multivariate PLS-R for most of the analytes. From the results obtained in this work, LIBS response varies depending on the element and the technique used for quantitative analysis. Simultaneous use of the univariate calibration curves with internal standard (intensity ratio) and PLS regression in multi-elemental analysis can help reduce the matrix effect of slags associated to their high variation in concentration. Overall, these results demonstrate the capability of LIBS as an alternative technique for analyzing gasification slags. Estimated limits of detection for Al, Ca, Fe, Si and V were 0.167, 0.78, 0.171, 0.243 and 0.01 wt.%, respectively.

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1. Introduction

Slag has been widely studied and proven useful in many industrial applications such as steel production and gasification. Slag analysis in metallurgical production processes increases steel quality by optimizing the chemical composition of slag; as the composition of a steel melt is greatly influenced by chemical reactions within the melt that can be seen within the slag components [1–3]. Slag analysis is also of great importance in some gasification processes where carbon feedstocks are converted into electricity, chemical products and transport fuel [4,5]. Environmental and economic challenges posed by the use of coal as feedstock, have called for alternatives such as petroleum coke (petcoke), biomass, and mixtures [6,7]. Development of reliable gasification technology depends on a good understanding of the influence of the feedstock mineral impurities on slag formation. Slag chemistry directly affects gasifier performance and its service life because of continuous interactions with protective lining materials during gasification and the viscous nature of the slag at exit. In some cases, slags could also be reused as a feedstock [8]. Chemical analysis of these slags is

often carried out using inductively coupled plasma-optical emission spectroscopy (ICP-OES) or simply ICP [9]. This technique requires time consuming sample digestion and has limitations for the analysis of refractory samples resulting in incomplete digestion. This technique is also limited by lack of inline capabilities, significantly slowing feedback. This can impact quality and productivity as it takes more time to make process and batch adjustments. X-ray fluorescence spectroscopy (XRF) is currently the state of art measuring technique for slags but the major difficulty with this technique is the well-known effects of absorption and/or enhancement related to the major element composition of samples and standards, as well as higher detection limits and the availability of suitable certified reference materials [10]. In order to reduce analysis time in favor of online analysis, there is a need to seek other analytical methods. Laser-based methods are of great interest for their simplicity and other features such as non-contact measurements with the analyte, less destructive, high measuring speed, and little or no sample preparation. Laser-induced breakdown spectroscopy (LIBS) is a spectrochemical analytical technique with the aforementioned features which permit multi-elemental analysis. LIBS has gained a lot of attention during the recent years as its scope of applications get wider from solid, liquid to gas analysis. There are a plethora of publications and books that elaborate on this versatile technique [11–13]. LIBS has previously been applied for multi-elemental analysis of slag samples from a steel plant and reported results were in agreement with XRF. Coefficients of determination R^2 of 0.99 for the main analytes Ca, Si and Fe

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of converter slags were achieved. Fast analysis of vacuum slag samples by LIBS was demonstrated for the first time in the steel works nearby a vacuum degasser station. LIBS analysis was achieved within 80 s with feasible further reduction. A representative analysis of SiO₂, CaO and Al₂O₃ of production samples without any further preparation was shown successfully in spite of the sample heterogeneity and variations in color, cracks and holes [1,3].

In the present work, considering the advantages offered by LIBS as mentioned above, the aim was to present LIBS as an alternative method of analyzing gasification slags by comparing LIBS results to those obtained by ICP-OES.

Synthetic slags with chemistry falling within coal–petcoke mixed feedstock slags were prepared for the investigation. Elements under investigation are Al, Ca, Fe, Si and V.

2. Materials and methods

2.1. Experimental setup

Fig. 1 shows the LIBS experimental setup. A frequency doubled second harmonic Q-switched Nd:YAG laser (Quantel CFR400 20 Hz, 7 ns pulse width, 6 mm diameter, 235 mJ maximum) was used as an excitation source. A small amount of a sample was applied to a double sided piece of tape that had been adhered to a glass slide. Once the sample was scattered onto the slide it was then placed on a rotating platform to ensure that the laser hit a fresh spot during each pulse. Laser beam was focused onto the sample surface through a 30 cm focal length quartz lens and a right angle prism. Spectra were collected with an Andor (Mechelle ME5000) broadband spectrometer (200–975 nm spectral range) through a 100 μm diameter optical fiber equipped with a pickup lens (Ocean Optics Inc. (OOI) Part No. 74-UV). The latter was placed 5 cm away from the sample and at 45° with respect to the beam axis. Andor Solis software was used for acquisition setup. The spectrograph was connected to a personal computer for data acquisition. All measurements reported herein were carried out with the same gate delay, gate width and laser pulse energy. These were respectively optimized to 3 μs, 10 μs and 67.5 mJ. All spectra correspond to the accumulation of 50 laser shots with each striking a fresh surface by rotating the sample. The resulting resolved spectra are used for qualitative and quantitative analyses. The plasma was characterized by evaluating the plasma electron density and temperature from the calcium emission lines. The analysis software packages Unscrambler X 10.3, OriginPro 2015, Veusz1.23.1 and excel 2013 were used for data analysis.

2.2. Methods

Quantitative analysis of LIBS is greatly affected by matrix effects and even more so when univariate calibration curves are used [13–15]. Self-

absorption and saturation are frequently observed and significantly influence the peak heights or areas of the analyte lines and thus affect the sensitivity of the curves from which unknown concentrations are to be derived [16–18]. Several methods have been used to correct the matrix effects [19–21]. In this work we apply internal standard and multivariate analyses (MVA) – partial least squares regression (PLS-R) to minimize the shot-to-shot fluctuations. The background corrected intensities used were selected according to Aydin et al. [22]. Atomic data of selected lines used for plasma characterization are referenced from NIST atomic data base [23]. Our results are compared with those obtained by ICP-OES.

2.2.1. Sample preparation

The elemental composition of the slag sample is listed in Table 1. Synthetic slags for this investigation were prepared following a procedure used by Nakano [24]. Reagent grade powders of respective oxides (Al, Ca, Fe, Si and V) were heated at 1425 °C for S1–7, 1575 °C for S8–12, and 1500 °C for the T1–4 series in a 64 mol% CO – 36 mol% CO₂ atmosphere for 3 days, followed by water quench. Upon water quenching, all the molten slags were vitrified. The samples were then dried and ground into fine powders. For ICP analysis a nominal mass of about 50 mg of the sample was fused with ~1 g of Li₂B₄O₇ and diluted to a final volume of 100 mL using 5% HNO₃ [25]; the analysis was performed using spectral lines Al 309.271, Ca 317.933, Fe 238.204, Si 251.611, and V 292.402. External calibration and internal standardization procedures [26] were utilized to quantify the analytes and based on the standard reference material (BIR-1) the accuracy of ICP analysis was within +7%. For LIBS analysis about 10 mg of powder sample was placed on a double sided adhesive tape glass slide.

3. Results and discussion

3.1. Plasma characterization

Plasma parameters such as temperature and electron density were evaluated. The Boltzmann plot (Fig. 2) for calcium lines Ca(II) 396.84 nm, Ca(I) 430.25 nm, and Ca(I) 443.49 nm (Table 2) yielded a temperature $T_e = (6000 \pm 300)$ K. Different ionization levels were used in order to avoid lines with close excitation energy. This was to limit the effect of varying spectral responses of the apparatus, as well as to minimize the sensitivity to small fluctuations in emission intensity [27]. Electron density of the laser-induced plasma ranged from 10¹⁶ to 10¹⁹ cm⁻³ and for this study, electron density was determined from Stark broadening which avoids the assumptions regarding local thermodynamic equilibrium (LTE) [27]. To determine the electron density of the plasma the spectral emission line for Ca (422.67 nm) was fitted using Lorentzian profile while the corresponding broadening coefficient

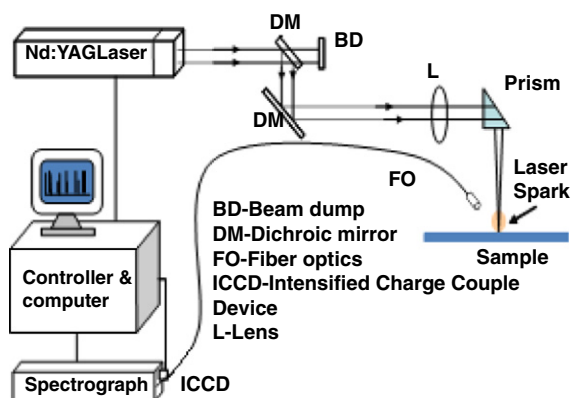


Fig. 1. LIBS experimental setup.

Table 1
Concentration ranges of analytes in slag samples analyzed by ICP-OES.

Sample (wt.%)	Al	Ca	Fe	Si	V
S1	14.12	6.01	4.85	29.62	0.01
S2	10.55	6.26	2.64	35.11	0.93
S3	23.86	6.05	5.37	21.66	0.01
S4	9.66	6.01	2.54	31.97	2.90
S5	13.69	6.19	1.60	26.37	3.69
S6	15.10	5.61	2.57	22.49	6.38
S7	14.19	7.21	1.44	34.15	3.29
S8	12.49	5.84	2.21	31.71	0.01
S9	25.69	6.86	3.07	24.38	0.02
S10	25.95	7.42	4.51	24.24	6.07
S11	17.32	5.89	3.27	24.12	1.61
S12	19.03	6.60	3.05	25.55	4.19
T1	24.14	5.23	13.86	53.39	0.03
T2	20.93	5.09	12.45	47.07	10.97
T3	17.51	5.08	11.39	39.92	23.04
T4	9.68	5.25	8.32	27.28	46.65
T5	6.49	5.18	6.72	19.72	59.35

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