



## Technical note

# Evaluation of the prediction precision capability of partial least squares regression approach for analysis of high alloy steel by laser induced breakdown spectroscopy



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## ABSTRACT

Laser induced breakdown spectroscopy (LIBS) was applied for elemental characterization of high alloy steel using partial least squares regression (PLSR) with an objective to evaluate the analytical performance of this multivariate approach. The optimization of the number of principle components for minimizing error in PLSR algorithm was investigated. The effect of different pre-treatment procedures on the raw spectral data before PLSR analysis was evaluated based on several statistical (standard error of prediction, percentage relative error of prediction etc.) parameters. The pre-treatment with "NORM" parameter gave the optimum statistical results. The analytical performance of PLSR model improved by increasing the number of laser pulses accumulated per spectrum as well as by truncating the spectrum to appropriate wavelength region. It was found that the statistical benefit of truncating the spectrum can also be accomplished by increasing the number of laser pulses per accumulation without spectral truncation. The constituents (Co and Mo) present in hundreds of ppm were determined with relative precision of 4–9% ( $2\sigma$ ), whereas the major constituents Cr and Ni (present at a few percent levels) were determined with a relative precision of  $\sim 2\%(2\sigma)$ .

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## 1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is an elemental analysis technique based on photon emission due to the de-excitation of excited atoms and/or ions (spectral emission) from laser-induced plasma. The technique provides rapid, in situ, simultaneous multi-elemental determination irrespective of the nature of the matrix [1,2], using standard based calibration methods [3,4] or theoretical calibration-free approaches [5]. LIBS is gaining popularity very fast for chemical analysis in solid matrix, due to the availability of very few direct analysis methods for solids (e.g., LA-ICPMS, GDMS, and XRF) [6,7]. With increasing acceptance of LIBS as a quantitative spectroscopic method for on-line industrial process control and measurement, there is a need for data analysis methods with high statistical significance. The quantitative analysis of LIBS spectra still remains a challenging task due to the overlapping emission spectrum, non-availability of proper calibration samples, matrix effects and especially pulse-to-pulse spectral variations [8–10]. Several methods have been proposed for calibrating the LIBS spectral data to the corresponding known elemental concentrations of

elements in standard samples with the goal of developing a model for quantitative analysis [11]. Conventionally, spectral peak intensity (peak area) is calculated in a LIBS spectrum and is used to construct calibration curves from matrix matched standard samples [12].

Steel is probably the most widely used material in the modern industrial regime. Several types of steels have been developed viz., stainless steel, low alloy steel, high alloy steel (HAS), borated steel, etc. Chemical analysis or checking of the steels is very important not only during their production stage but also during the life time to check for degradation. Chemical analysis of steels is focused on both impurities and doping components concentrations. HAS offers a wide range of properties with respect to ductility, hardness, corrosion resistance, machinability, thermal and electric conductivity, etc. About 95 wt.% of the total elemental content in HAS is contributed by Fe, Cr and Ni. The motivation of this work is the economic and technical importance of HAS in the nuclear industry. In HAS, the Cr content is usually  $> 11$  wt.% and this allows formation of a passive surface oxide that prevents oxidation and corrosion. HAS also has good resistance to oxidation, even at high temperatures. Some high chromium alloys (25 to 30 wt.%) can be used at temperatures as high as 1000 °C. A few examples of HAS used in nuclear industry are a) AISI 403, AISI 410, Sandvick Sweden HT9, Sandvick Sweden HT7, French R8, French EM12, Japanese HCM9M etc. in turbine

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blades and end fittings in pressurized heavy water reactor (PHWR); b) JPCA, 316Ti, 15-15Ti, PNC 1520, FV548 etc. as in-core materials in fast breeder reactors; c) 316 SS, M316, PE 16, HT 9, etc. as fuel clad materials in various countries; and d) 316 L(N), 316FR and 316LN in European Fast Reactor (EFR), Demonstration Fast Breeder Reactor (DFBR) and in Super-phenix reactor [13,14]. There are many direct solid sample analysis techniques reported in literature for steel among them, XPS can analyze Cr with 10–20% accuracy and ~5% precision [15]; SF-ICP-MS can analyze Co, Cr, Mn, Ni with 2–6% precision [16]; and Scanning Proton microprobe-X-ray can analyze Cr, Mn, Co, Ni and Mo with 2–6% accuracy and 2–15% precision [17]. LA-ICP-AES/MS has also found great success in steel analyses for all the elements with a precision and accuracy of 5–10% [18].

Investigations on different types of HAS by LIBS have been reported in literature by different groups. Cabalin et al. studied the influence of laser light wavelengths on the analytical performance for determining the elements Si, Ti, Nb and Mo [19]. Palanco et al. developed an instrument for fast quality assessment in the steel, and also analyzed stainless steel samples at high temperatures in air at atmospheric pressure [20, 21]. Identification of high-alloy steel grades of pipe fittings for routine industrial operation was developed by Noll et al. [22]. Bassiotis et al. quantified Ni, Cr, and Mn in HAS using Fe as an Internal Standard (IS) [8]. Quantification and comparison of nine elements by single and double pulse LIBS were carried out by Vrenegor et al. at two laser pulse energies [10]. Lopez-Moreno et al. analyzed low alloy steel with a portable microchip LIBS instrument [23]. All these above mentioned works have used univariate calibration method applying internal standard approach, which requires data on the concentration of Fe in the unknown samples. Prior knowledge of Fe concentration is often not possible especially in industrial setting for the unknown samples [24]. Thus, there is a need to develop other calibration methods/models.

Multivariate calibration does not require knowledge of the major matrix element concentration in the unknown samples. There are a few literature reports on the application of statistical procedures like artificial neural network (ANN), principle component regression (PCR), partial least squares regression (PLSR), etc. on the LIBS spectra in biological, geological, forensic analysis [25–28]. There have been limited reports on the application of multivariate approach on LIBS application for steel. Stipe et al. compared the IS based univariate method with PLSR on the major metallic components (Cr, Ni, Mn) of steel using 15–20 nm portions of spectra [24]. The report showed that IS method and PLSR generate almost similar analytical results. Sorrentino et al. showed that the PLSR for Si using 287.1–288.6 nm generates results with poor accuracy [29]. Zaytsev et al. applied PCR for steel analysis using different wavelength regions of spectra for Cr, Ni, Mn and Si and demonstrated better prediction capabilities for multivariate approach than IS method [30]. Gonzaga et al. using also a low resolution, time-integrated detection for analyzing HAS, predicted Cr, Ni and Mn concentrations using PLSR [31,32]. Gu et al. also used PLS for Cr and Ni determinations by LIBS with PLS [33].

The primary goal of the present work was to statistically evaluate the PLSR approach for analyses of HAS samples for quantification of Cr, Ni, Mn, Si, Co and Mo. Effects of laser pulse accumulation and spectral data pre-treatment procedures were studied. Different models representing different sets of wavelength ranges were also studied. The manuscript reports a detailed discussion on the analytical performance of steel analysis by PLSR approach to achieve <2% ( $2\sigma$ ) for major and <5% ( $2\sigma$ ) relative precision for minor constituents, along with the effect of LIBS spectral resolution.

## 2. Experimental

### 2.1. LIBS system and measurements

The experimental setup is similar to the one previously described [34]. Briefly a frequency-doubled Nd:YAG laser (532 nm) (Continuum

Surelite III-10) capable of delivering a maximum energy of 425 mJ (energy variance of ~4%) with a pulse duration of 4 ns and a maximum pulse repetition rate of 10 Hz was focused through a fused silica lens of focal length 15 cm onto the sample surface. The spot size of laser ablation was 300  $\mu\text{m}$ . The laser induced plasma emission was collected at an angle of 45° to the incident laser beam by an optical fiber bundle coupled to a spectrometer (Ocean Optics, LIBS 2000+) equipped with a charge-coupled device (CCD). The LIBS spectra were recorded employing a spectral resolution of 0.1 nm in the spectral range of 200–500 nm. All the spectra were recorded in open atmosphere. The operating parameter of CCD was set at 1.5- $\mu\text{s}$  gate delay which is fixed in the instrument and cannot be altered. Laser pulse energy was measured with an energy meter (Genetec-e model UP19K-30H-VM-DO). Laser energy of 30 mJ was used in this study and this generates a laser irradiance of 10 GW/cm<sup>2</sup> which is sufficient for production of a plasma.

### 2.2. Sample

Ten certified high alloy steel samples, provided by BAM, Berlin ([www.bam.de](http://www.bam.de)) in the framework of the LIBS 2008 Interlaboratory Comparison were used. The composition of the certified samples was provided by BAM as reported in Table 1. The Contest was aimed to assess current analytical capabilities of the LIBS technique [35]. Fe concentration was not provided and hence was calculated knowing the other major constituents. But due to the presence of some non-negligible unreported elements, there can be uncertainty in Fe concentration [29]. For Si, C8 sample was not used as the concentration of Si in C8 is much higher than the concentrations in the other samples in the set and this will generate an erroneous regression result.

### 2.3. Analysis

The LIBS spectra recorded by LIBS 2000+ were subjected to truncation of first and last 50 pixels for eliminating the errors arising due to poor quantum efficiency of the detector. For optimization and comparison of different experimental parameters, triplicate analyses of all the 10 standard samples were performed considering four different laser pulse accumulation conditions (10, 30, 60 and 100 pulses). For comparing different pretreatment procedures (Section 3.2), spectral data were pre-treated as per respective conditions before utilizing PLSR approach. After detailed comparison of different analytical approaches or models, the selected model was extensively evaluated again with the ten HAS samples re-analyzing each 10 times. These samples were arranged in two sets before performing PLSR. Calibration set (CS) consisting of 7 samples was used for constructing calibration curves and a validation set (VS) consisting of 3 samples was used for validation of the calibration models. The number of samples in VS is small compared to that of CS for evaluating the performance of LIBS for HAS in general. But non-availability of a large number of standard samples of HAS forced us to

**Table 1**  
Certified composition of the BAM provided steel samples.

Samples	Elemental concentration (wt.%)							
	C	Mn	Si	Ni	Cr	Mo	Co	Fe
C1	0.092	0.74 <sup>a</sup>	0.46	12.55	12.35	–	–	73.81
C2	0.0103	0.686	0.374 <sup>a</sup>	6.124	14.727	0.0138	–	78.06
C3	0.0345	0.722	0.463	12.85 <sup>a</sup>	11.888	0.0304	–	74.01
C4	0.019	1.4 <sup>a</sup>	0.27	10.2 <sup>a</sup>	18.46 <sup>a</sup>	0.265	0.116	69.27
C5	0.086	0.791	0.57	20.05	25.39	–	0.054 <sup>a</sup>	53.06
C6	0.066	1.38 <sup>a</sup>	0.405 <sup>a</sup>	9.24	17.31	0.092	0.053	71.45
C7	0.0141	1.311	0.48 <sup>a</sup>	10.2	17.84	2.776	0.0184	67.36
C8	0.143	1.7	1.41 <sup>b</sup>	8.9 <sup>a</sup>	17.96	–	0.018	69.87
C9	0.05	0.89	0.21	5.66	14.14 <sup>a</sup>	1.59	0.22	77.24
C10	0.0201	1.745	0.537	10.72	16.811 <sup>a</sup>	2.111 <sup>a</sup>	0.0525	68.00

<sup>a</sup> VS samples.

<sup>b</sup> Not a part of CS for Si.

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