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Comparison of spectrum normalization techniques for univariate analysis of stainless steel by laser-induced breakdown spectroscopy

VIJAY KARKI[1], ARNAB SARKAR[1,*], MANJEET SINGH[1],
GULAB SINGH MAURYA[2], ROHIT KUMAR[2],
AWADHESH KUMAR RAI[2] and SURESH KUMAR AGGARWAL[1]

[1]Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[2]Department of Physics, University of Allahabad, Allahabad 211 002, India
*Corresponding author. E-mail: asarkar@ymail.com; arnab@barc.gov.in

Abstract. Analytical performance of six different spectrum normalization techniques, namely internal normalization, normalization with total light, normalization with background along with their three-point smoothing methods were studied using LIBS for quantification of Cr, Mn and Ni in stainless steel. Optimization of the number of laser shots per spectrum was carried out to obtain the best analytical results. Internal normalization technique model was used for selecting the best emission lines having sufficient intensity and spectral purity for Cr, Mn and Ni for comparison of different normalization techniques. For detailed evaluation of these normalization techniques, under optimized experimental conditions, three statistical parameters i.e., standard error of prediction, relative standard deviation and average bias, were compared for these techniques using the selected emission lines. Results show that the internal normalization technique produces the best analytical results followed by total light normalization. The smoothing of the raw spectra reduces the random error and produces better analytical results provided the peak under study has sufficient (≥ 7) number of pixels.

Keywords. Laser-induced breakdown spectroscopy; univariate study; normalization models; stainless steel; standard error of prediction.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is an experimental characterization technique for the qualitative and quantitative analysis of the samples. In this technique, a high-power laser beam is focussed by converging through a lens on the sample surface. The high energy density of the laser beam ablates the material and forms transient plasma by multiphoton ionizations and collision cascades route [1–3]. The emission from the plasma

is collected by the collection optics and is analysed, which provides qualitative and quantitative description of the sample composition. Due to several advantages offered by the LIBS measurements over other conventional techniques (e.g., inductively coupled atomic emission spectroscopy, X-ray fluorescence, etc.) such as minimal sample preparation, non-contact analysis, non-destructive nature, minimum sample requirement, applicability to detect and measure all the elements of the periodic table [4–9] and comparative fast analysis in real time, this technique has gained popularity in several fields such as industrial [10–12], medical [13], biological [14], pharmaceutical [15], archaeological [16], environmental [17], nuclear [18–20], forensics [21] etc.

Research is going on for improving the analytical capabilities for determining elemental composition by LIBS for the last three decades [22–25]. In LIBS analysis, the spectral intensities obtained under the same experimental conditions from a given sample can have significant variations due to several factors like laser energy instabilities, surface inhomogeneities, laser–sample interactions, etc. Different spectral normalization and standardization techniques are reported in the literature for the optimization of these fluctuations. Adrain and Watson employed the matrix element normalization method (also known as internal normalization method) for constructing the calibration curve and this method is widely used [26]. Guo *et al* showed improved results for quantitative analysis of V, Cr and Mn through calibration curves using the internal normalization technique [27]. Huang *et al* compared single-line calibration, normalized with total light of the raw spectra as well as with smooth processing of spectra for the detection of Cr in the water samples using Cr(I) 425.43 nm emission line. The spectral normalization against total light on smoothing preprocessed spectra gives better accuracy and precision than raw spectra analyses and is also better than total light normalization. By single-line calibration, intensity ratio calibration with raw data and smooth processing, the accuracy values were determined as 13.2, 11.7 and 10.8% respectively [28]. Zou *et al* proposed a modified algorithm based on wavelet transform of background subtraction for the quantitative analysis of the four elements Cr, V, Cu and Mn in low alloy steel samples using LIBS [29]. Stipe *et al* used LIBS on 23 low to high alloy steel samples to quantify the concentrations of Cr, Ni and Mn. Three calibration methods, peak area integration normalized by an internal standard, peak area normalized by total light and partial least squares technique, were used in the study. They found that the performance of partial least squares is on par with using iron as an internal standard [30]. Many other spectral normalization techniques are reported in literature using plasma temperature, electron number density, degree of ionization, etc [31]. Among all these normalization techniques proposed, the internal normalization method remains the most popular normalization technique. However, the method suffers from a major drawback that the major matrix element concentration must be the same or need to be known in all the samples before LIBS analyses, which is not feasible at all times especially in the case of unknown samples.

Steel is one of the major components of metallurgical industries. Due to its wide industrial applications, the compositions vary depending on the target applications. Thus, the concentrations of these elements must be determined precisely and accurately. In the present work, we tried to compare six normalization techniques for LIBS spectral analyses to quantify Cr, Mn and Ni in high alloy stainless-steel samples. The paper reports a detailed discussion on the analytical performance of steel analysis by different normalization techniques in LIBS based on multiple statistical parameters.

2. Experimental

The present study was carried out in an open atmospheric experimental set-up, having 532 nm frequency doubled Nd:YAG laser (Continum SureliteIII-10) producing 4 ns pulse with 10 Hz repetition rate. The laser beam was focussed by a fused silica lens of focal length 30 cm on to the sample surface. A fixed laser pulse energy of 30 mJ was used for the present analysis. The emission from the transient plasma was collected by an optical fibre bundle and was fed to a spectrometer (Ocean Optics, LIBS 2000+) equipped with a CCD. The CCD was fixed with a constant gate delay of 1.5 μs. The spectrometer has a resolution of 0.1 nm at 300 nm, covering a spectral range of 200–500 nm. The univariative study of different normalization models was carried out on the 10 certified high alloy stainless-steel samples provided by BAM on the framework of the LIBS 2008 contest [32]. The concentrations of Cr, Mn and Ni in the samples are given in table 1. Fe concentration was calculated by knowing the other reported elemental concentrations.

For optimizing the number of single-shot spectra accumulation per LIBS spectrum, triplicate analyses of all the standard samples were carried out for 10, 30, 45, 60, 80 and 100 shots separately. The samples C1–C10 were arranged in two sets: calibration set (CS) consisting of seven samples used for constructing the calibration curves based on different normalization techniques and test set (TS) consisting of three samples used for validation of these calibration models. The TS samples were selected in such a way that the concentrations of different elements lie between the minimum and maximum concentration dynamic ranges of CS to minimize the fitting error arising due to least squares fitting. The superscript t in table 1 represents the TS samples chosen for different elements, while the remaining were the CS samples. After optimizing the number of laser shot accumulation, for detailed evaluation of different normalization models, 10 replicate analyses were again performed under optimized conditions on each sample for comparing the analytical capabilities of the different normalization models.

Three statistical parameters, namely standard error of prediction (SEP), relative standard deviation (%RSD) and average bias or accuracy (i.e., the closeness of the agreement

Table 1. Certified composition of Cr, Mn, Ni and Fe in steel samples provided by BAM.

Samples	Elemental concentration (wt%)			
	Mn	Ni	Cr	Fe
C1	12.35	12.55	**0.74^t**	73.81
C2	14.727	6.124	0.686	78.06
C3	11.888	**12.85^t**	0.722	74.01
C4	**18.46^t**	**10.2^t**	**1.4^t**	69.27
C5	25.39	20.05	0.791	53.06
C6	17.31	9.24	**1.38^t**	71.45
C7	17.84	10.2	1.311	67.36
C8	17.96	**8.9^t**	1.7	69.87
C9	**14.14^t**	5.66	0.89	77.24
C10	**16.811^t**	10.72	1.745	68

^{t}TS samples for the elements in the column.

between the result and the true value) were considered for the evaluation of different normalization models [28,33].

$$\text{SEP} = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (C_s - C_p)^2}, \tag{1}$$

$$\%\text{RSD}(i) = \frac{1}{N} \sum_{1}^{N} \sqrt{\frac{1}{j} \sum_{i=1}^{j} (C_p - C_m)^2} \times 100/C_m, \tag{2}$$

$$\text{Average bias (\%) or accuracy (\%)} = \frac{1}{N} \sum_{i=1}^{N} \frac{(C_s - C_p)}{C_s} \times 100. \tag{3}$$

Here, N represents the total number of TS samples, C_p, C_m, C_s represent the predicted, average and standard concentration of the TS samples respectively. J is the number of replicate analyses, which is 3 or 10 in the present case. SEP is a type of mean square error and has two components, and is equal to the sum of variance or precision and the squared bias or accuracy. The second component of SEP is different from the bias in eq. (3) which is the average bias of all analyses and can have both positive and negative values unlike the previous one. The smaller the SEP, better is the analytical capability.

3. Spectral normalization models

Six normalization techniques were compared in the present study. These were: (i) internal normalization (IN), (ii) normalization with total light (NTL), (iii) normalization with background (NB), (iv) internal normalization after smoothing (INS), (v) NTL after smoothing (NTLS), (vi) NB after smoothing (NBS). The techniques (i) [20,26,34], (ii) [30,31] and (iii) [35] (v) [28], have already been reported in the literature. Techniques (iv) and (vi) are implemented first time for spectra normalization in this study, to the best of our knowledge. The details of these methods are discussed below:

Internal normalization (IN): IN technique is the most commonly used and reported technique in literature. It is used to overcome the uncertainty and fluctuations in the spectra, by normalizing the emission line intensity of the analyte element of interest, with a reference element intensity, preferably the matrix element or the most abundant element of the matrix. Under local thermodynamic equilibrium (LTE), the natural logarithm of the intensity ratio of a spectral line emitted by an analyte element (denoted by the subscript a) to that emitted by the internal standard element (denoted by the subscript r) considered in the IN method, is given as

$$\ln\left(\frac{I_a}{I_r}\right) = \ln\left(\frac{N_a}{N_r}\right) + \ln\left(\frac{g_a A_a Z_r \lambda_r}{g_r A_r Z_a \lambda_a}\right) - \left(\frac{(E_a - E_r)}{kT}\right). \tag{4}$$

Here, I, N and Z represent the intensity of the spectral lines, total number density and partition function, respectively. E, g, A and λ are the energy, degeneracy of the upper

level, transition probability and wavelength, respectively, for the observed line transitions, k is the Boltzmann constant and T is the plasma temperature. Thus, the plot of natural logarithm of the intensity ratio vs. the natural logarithm of the concentration ratio is a straight line with a slope of unity, provided that, the temperature and other plasma parameters remain constant. However, in practice, this is not always feasible. Therefore, to minimize the fluctuations in the last part of the intercepts, only those emission lines of the analyte and reference element which have very small difference in the upper energy levels compared to kT were selected.

Normalization with respect to total light (NTL): The main limitation of the IN technique is that the concentration of the reference element must remain constant in the entire sample sets or the concentration must be known which is not always possible. To overcome this limitation, the peak intensity area of the analyte of interest is normalized with the whole spectrum area or total light, thereby eliminating the pre-requirement of knowing the concentration of the reference element i.e., internal standard.

Normalization with background (NB): In this normalization technique, the peak area of the analyte is normalized with the background intensity of the peak. The background height was calculated by fitting the peak with a Gaussian peak. The width of the background, i.e., the number of pixels in the background calculation was the same as the width i.e., number of pixels of the peak of interest.

Internal normalization after smoothing (IN-S): The LIBS spectra are also accompanied by random errors, which can be minimized only if the average or accumulated spectra of a very large number of shots are considered for analysis, which is not always experimentally feasible. In order to eliminate such errors, spectral pre-processing can be applied. Smoothing method is one of these methods in which each data value is replaced with the average of neighbouring data values. In equation form, smoothing of data point is given as

$$Y_i = \frac{1}{(2m+1)} \sum_{j=-m}^{m} Y_{i+j}, \tag{5}$$

where Y_i represents the intensity of the smoothed data point and Y_{i+j} represents the intensity of raw data points of the spectrum. In this model, the raw spectra were smoothened by applying the three-point smoothing algorithm ($m = 1$) followed by the IN model.

Normalization with total light after smoothing (NTL-S): In this normalization technique, three-point averaging was performed on the raw data and then the spectral emission line intensity was normalized with total light intensity as discussed in the previous section.

Normalization with background after smoothing (NB-S): Same technique as mentioned in section NTL-S was used here but instead of NTL, NB method was applied after smoothing.

4. Results and discussion

For optimization of the number of laser shots per analysis, SEP and RSD were calculated for three prominent emission lines of Cr, Mn and Ni observed in the LIBS spectra, (Cr(I)
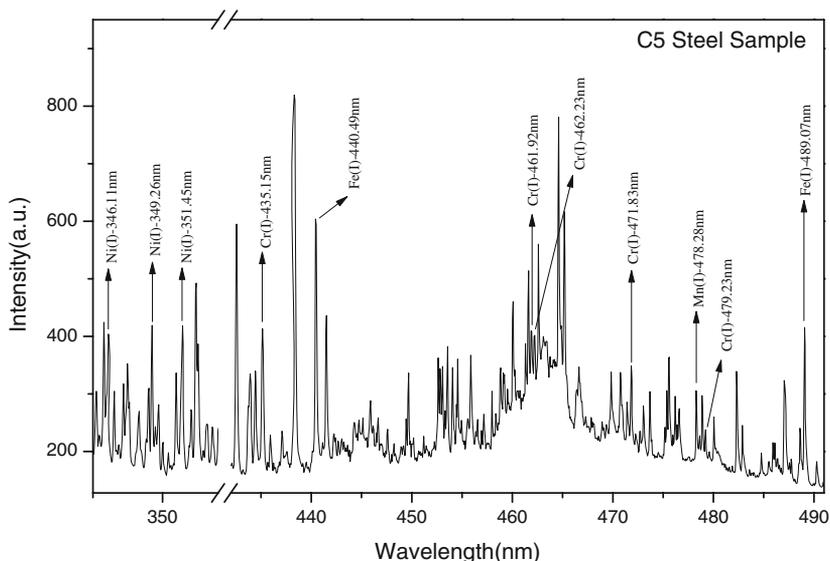
Figure 1. Typical LIBS spectra of the C5 steel sample under experimental conditions.

461.95 nm, Mn(I) 478.34 nm and Ni(I) 345.84 nm). Figure 1 shows a typical LIBS spectrum of steel under experimental conditions. Among the six normalization techniques mentioned previously, the IN model is the most widely reported method in the literature. Therefore, this technique was used for optimization study. Fe(I) 489.14 nm, Fe(I) 440.47 nm and Fe(I) 346.58 nm emission lines were used for the normalization of Cr, Mn and Ni emission lines, respectively. Figure 2 shows the variation of SEP for the
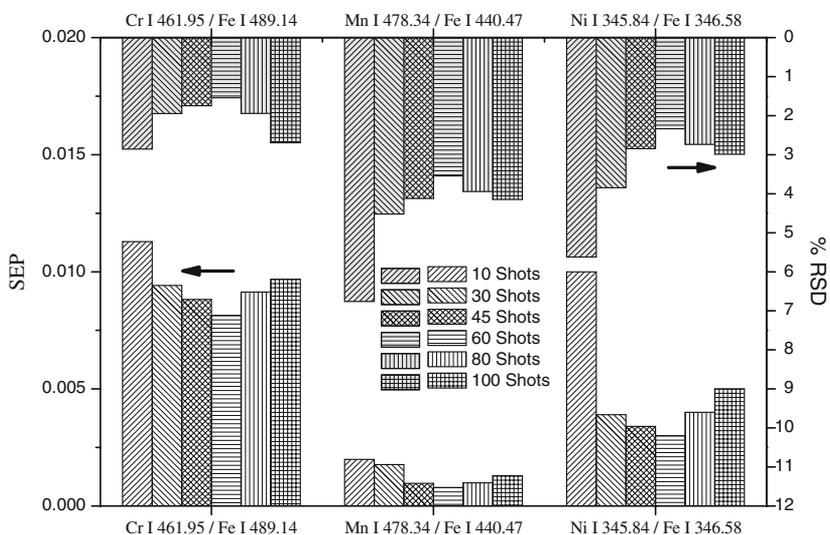
Figure 2. Variation of SEP and RSD with the number of average shots for atomic line ratios of Cr, Mn and Ni normalized with Fe.

normalized emission lines against the number of average shots carried out for the TS samples, using the CS samples for calibration curves. The respective %RSD obtained for these normalized lines are also shown in figure 2. Both the parameters show a minimum for 60 shots accumulation, indicating a global minimum at 60 shots. Similar trend was also observed for ionic emission lines of these elements. Hence, accumulated spectra of 60 shots were chosen for further analysis as an optimized parameter. This is contrary to the common practice of using a large number of laser shots per analysis. The poorer SEP and RSD at 80 and 100 shots analysis is attributed to the fact that with more analysis at the same position, crater effect becomes a dominant factor degrading the analytical performances. The spectra obtained for 60 laser shots accumulation were used for the

Table 2. Selected emission lines of Cr, Mn, Ni with corresponding normalizing Fe lines chosen for internal normalization. Values in bold represent the emission lines of the element chosen for final comparisons of different normalization methods.

Analyte element	Ionization state	Emission line (nm)	Normalizing Fe line (nm)	Abbreviation for the ratio
Cr	(I)	359.35	375.82	
		435.17	**440.47**	Cr(I)-a
		461.95	**489.14**	Cr(I)-b
		462.24	**489.14**	Cr(I)-c
		471.84	**489.14**	Cr(I)-d
		479.25	**489.14**	Cr(I)-e
	(II)	**265.85**	**272.75**	Cr(II)-a
		275.89	**275.32**	Cr(II)-b
		284.32	**272.75**	Cr(II)-c
		312.49	274.64	
Mn	(I)	**476.23**	**489.14**	Mn(I)-a
		476.64	**489.14**	Mn(I)-b
		403.07	395.66	
		478.34	**440.47**	Mn(I)-c
		475.40	440.47	
	(II)	**344.19**	**274.64**	Mn(II)-a
		294.92	274.64	
		293.93	**274.64**	Mn(II)-b
		257.61	**258.58**	Mn(II)-c
Ni	(I)	**341.47**	**346.58**	Ni(I)-a
		356.63	358.11	
		361.93	374.82	
		351.50	**371.99**	Ni(I)-b
		349.29	**346.58**	Ni(I)-c
		346.16	**346.58**	Ni(I)-d
		345.84	**346.58**	Ni(I)-e
	(II)	**231.60**	**256.25**	Ni(II)-a
		241.61	**275.32**	Ni(II)-b
		239.45	275.32	

selection of Cr, Mn and Ni emission lines. As a significant amount of interference was present in the spectral lines mainly due to Fe and other elements present in the steel samples, emission lines of these elements were carefully selected by comparing with the NIST database [36]. This procedure identified 46 atomic and 15 ionic emission lines of Cr, 7 atomic and 3 ionic lines of Ni, 5 atomic and 4 ionic lines of Mn. Due to large numbers of Cr emission lines, further refinement was carried out by applying the following two criteria: (1) spectral purity (i.e., having no interferences from other peaks within ± 0.3 nm) and (2) sufficient intensity (≥ 100 a.u. signal height), which lead to only 6 atomic and 4 ionic lines of Cr. For IN model, the Fe, Mn, Ni lines were also selected by following the above-mentioned criteria. Table 2 shows 29 emission lines of Cr, Mn and Ni along with the normalizing Fe lines chosen for the IN model.

For comparing different normalization models, the number of atomic and ionic emission lines of Cr, Mn and Ni were further reduced by selecting only those lines having less SEP and high R^2 for the IN model. Figure 3 shows the variation of statistical parameters for atomic line ratios of Mn normalized with Fe atomic lines. The downward arrows point towards the selected normalized ratios having low SEP with high R^2, chosen for further evaluations. Similar study was used for the selection of different emission lines for Cr(I), Cr(II), Mn(II), Ni(I) and Ni(II). Five atomic and three ionic emission lines of Cr, three atomic and three ionic emission lines of Mn, five atomic and two ionic emission lines of Ni were selected. These emission lines are shown in bold in table 2 and were employed for comparing different normalization models. None of the emission lines chosen were found to show any self-absorption.

For detailed comparison of different normalization models and for achieving better analytical results (i.e., good accuracy and precision), ten replicate analyses were performed
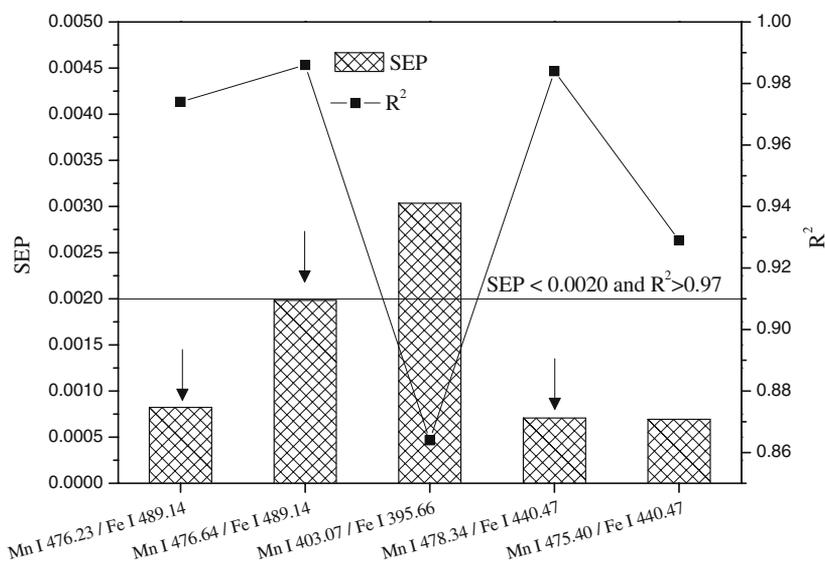

Figure 3. Variation of statistical parameters (SEP and R^2) of different IN models for Mn atomic lines. Arrows show the shortlisted atomic lines of Mn(I) selected for further study.

on each of the three TS samples as discussed previously and were analysed by the calibration curves of different normalizations. The obtained results were compared with the reference values mentioned in table 1. Figures 4 and 5 respectively show the variations of statistical parameters of different normalization models for atomic and ionic emission lines of Cr. It can be seen from figures 4 and 5 that both the IN and IN-S methods have the best analytical capabilities compared to the other four methods. The NTL and NTL-S methods closely follow the IN and IN-S methods. The NB and NB-S models generate the worst statistically relevant results, which is expected as the fluctuations in the background are higher compared to the TL and the fitting procedure for background calculation may also not have been accurate. To calculate the area under a peak, first the peak centre was identified and then in both the left and right sides, the first pixel having intensity $\leq \pm 5$ a.u. from background, was selected as lower limit and upper limit of the peak as shown in figure 6 for Cr(I) 435.17 nm. In general, it was observed that pre-processing spectra with smoothening method do not affect the analytical capability of the normalization techniques (i.e., IN, NTL and NB) to any noticeable extent. It was also noticed that if the number of pixels or points inside an emission peak under consideration is ≥ 7, then the 3-point smoothing is effective in decreasing the errors, thereby improving the average bias(%) and RSD(%). But if the points are lesser, then smoothing has arbitrary effects. For e.g., Cr(I) 435.17 nm emission line has eight pixels in the peak and hence irrespective of the normalization technique, smoothing spectra results give better average bias(%) and RSD(%). For atomic lines of Cr, Cr(I)-a ratio, i.e., Cr(I) 435.17 nm/Fe(I) 440.47 nm gives the best average bias(%) and RSD(%) of ~2.5% and ~2%, respectively, using IN technique. In the case of NTL and NTL-S normalization
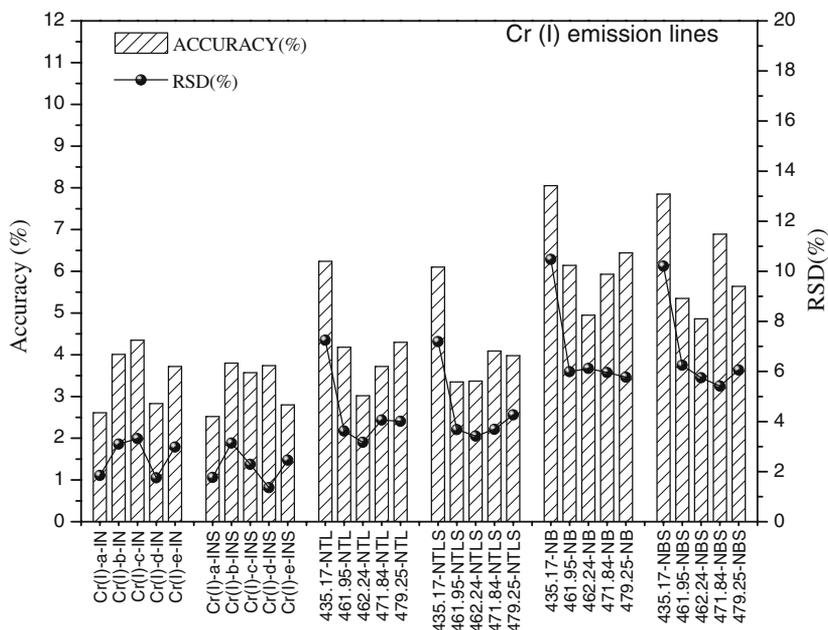

Figure 4. Comparison of average bias and %RSD of selected emission lines of Cr(I) with different normalization models.
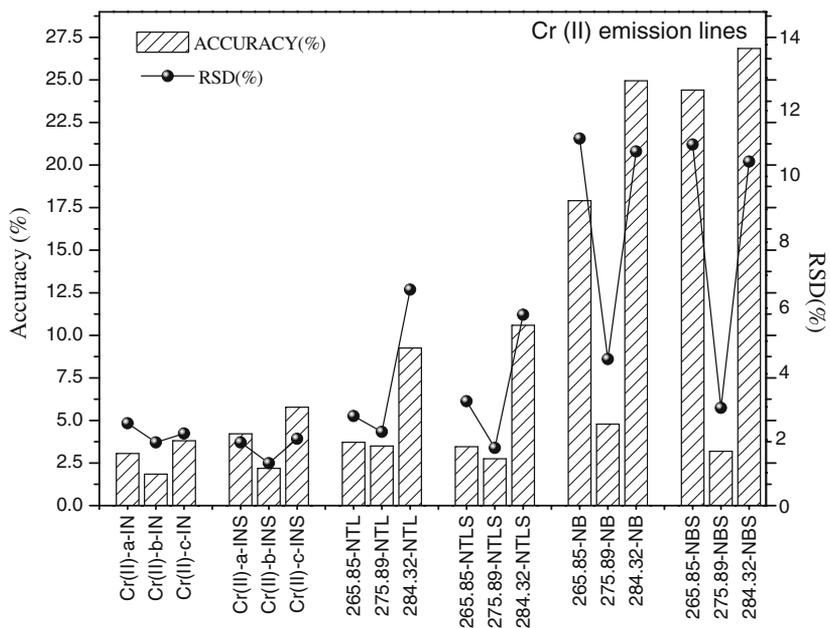
Figure 5. Comparison of average bias and %RSD of selected emission lines of Cr(II) with different normalization models.
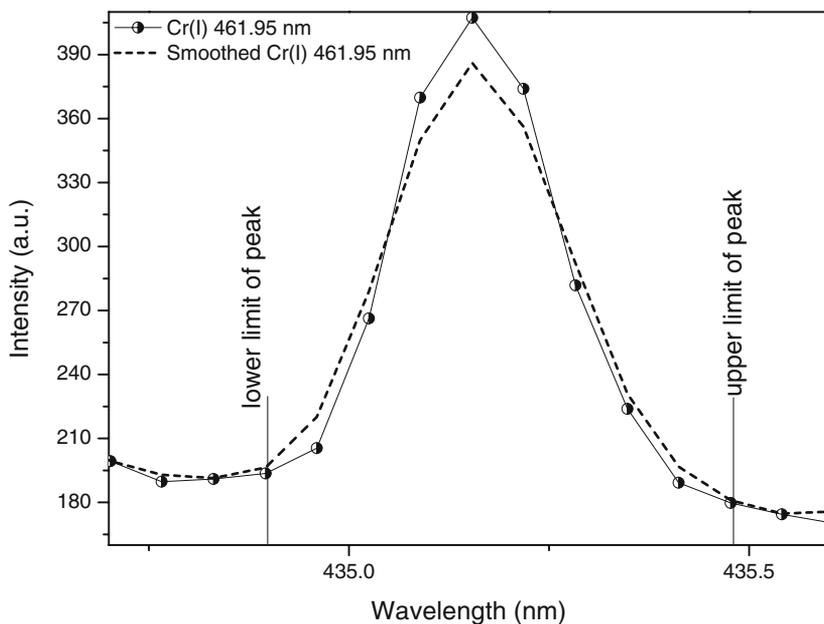

Figure 6. Cr(I) 435.17 nm emission line along with the lower and upper limits for peak area calculation.
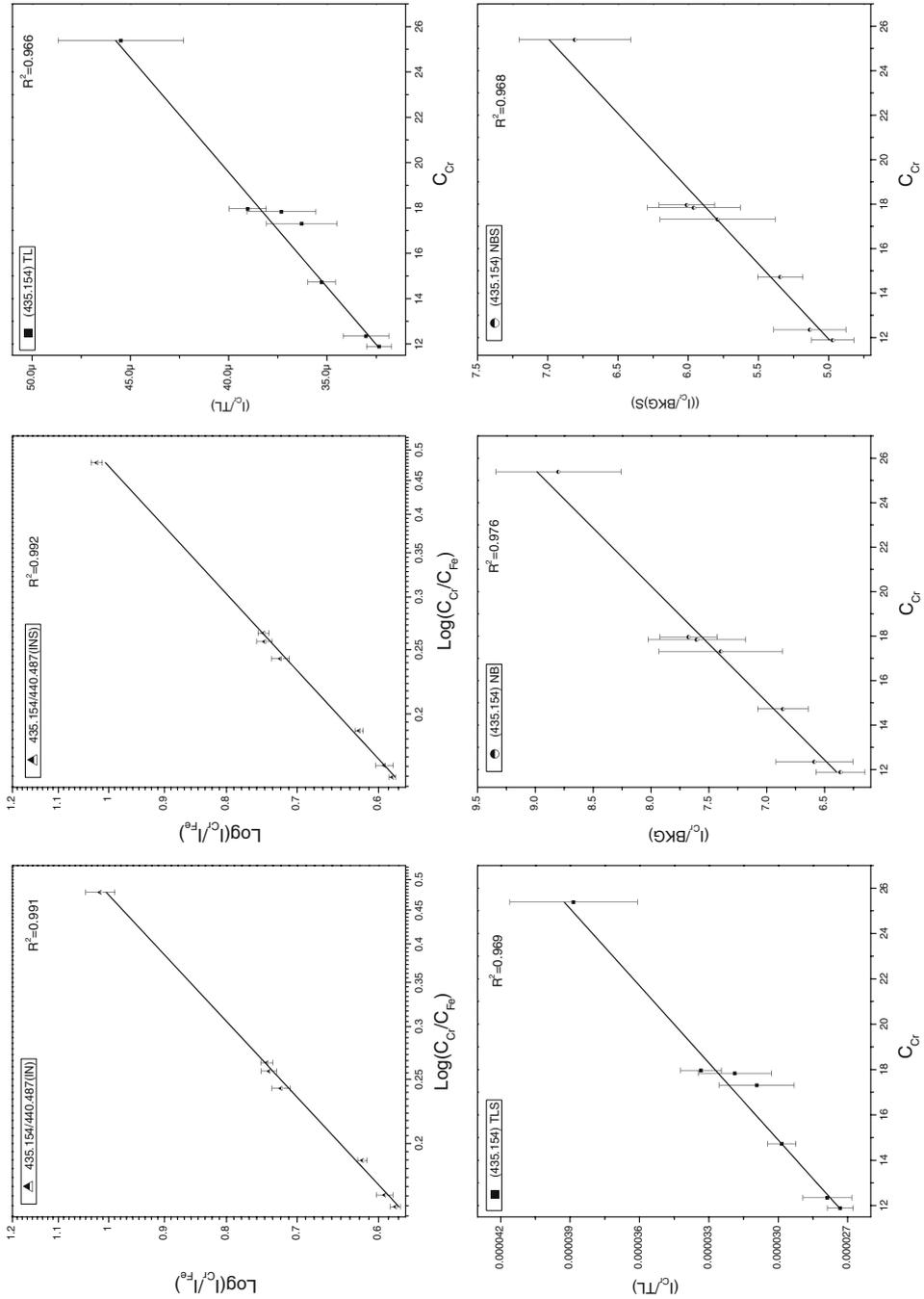
Figure 7. Comparison of the six types of calibration curves from the Cr(I) 435.17 nm line.

models, Cr(I) 462.24 nm has ∼3% average bias(%) and RSD(%). For NB and NB-S, the best result was ∼5% average bias(%) and RSD(%) for Cr(I) 462.24 nm again. For ionic lines of Cr, the best line was Cr(II) 275.89 nm, in all the six normalized models with best average bias(%) and RSD(%) of ∼1.8% for IN model followed by 2.7% for NTL method. The results obtained by all these six normalized methods are found to be better than the results obtained using only raw data with no normalization procedure, which has ∼13–15% accuracy and precision. This indicates the importance of normalization technique. Figure 7 shows a comparison of the six types of calibration curves from the Cr(I) 435.17 nm line.

The analytical capabilities of Ni(I) and Ni(II) emission lines were also studied. Figure 8 shows the results obtained for Ni(I) for different normalization models. As shown in figure 8, only IN and IN-S models give better analytical results than TL, TL-S, NB and NB-S models. The Ni(I)-b (Ni(I) 351.50 nm/Fe(I) 371.99 nm) shows the best analytical results with an average bias(%) of ∼2.3% and RSD(%) of ∼2% in IN technique. However, for the NTL and NB methods, the Ni(I) 346.16 nm shows poor performance. In NTL method, Ni(I) 346.16 nm produced results with an average bias of 5% with 3% RSD(%). For Ni(II), the IN and TL models along with their smoothing models give better analytical results compared to NB and NB-S models. Overall, the best results were obtained with INS normalization technique for Ni(II)-a (Ni(II) 231.60 nm/Fe(II) 256.25 nm) with an average bias of ∼3% and RSD(%) of ∼2 %.

Figure 9 shows the comparison of average bias(%) and RSD(%) of different normalization models for Mn(I) emission lines. Both Mn(I) 476.23 nm and Mn(I) 476.64 nm have significant interference from matrix emission lines. Hence, in these cases, we have taken
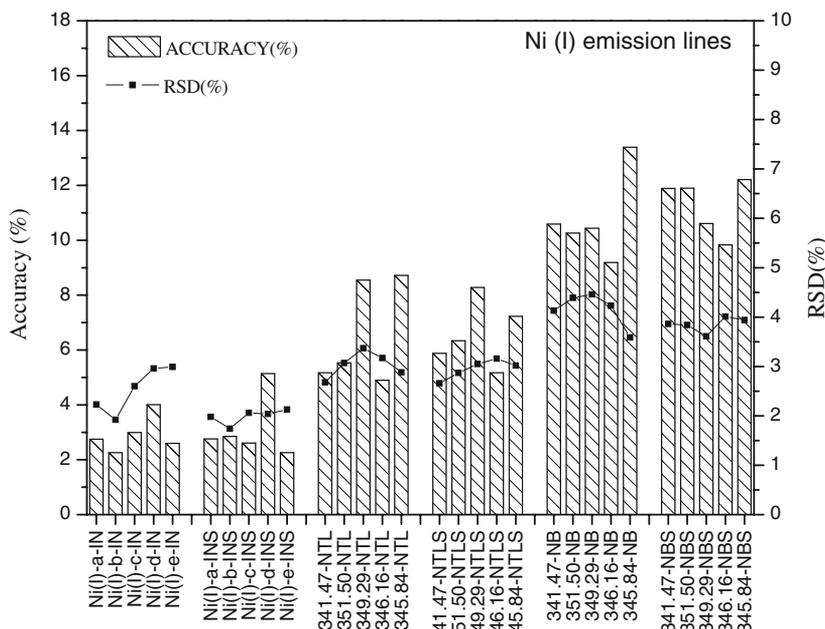

Figure 8. Comparison of average bias and %RSD of selected emission lines of Ni(I) with different normalization models.
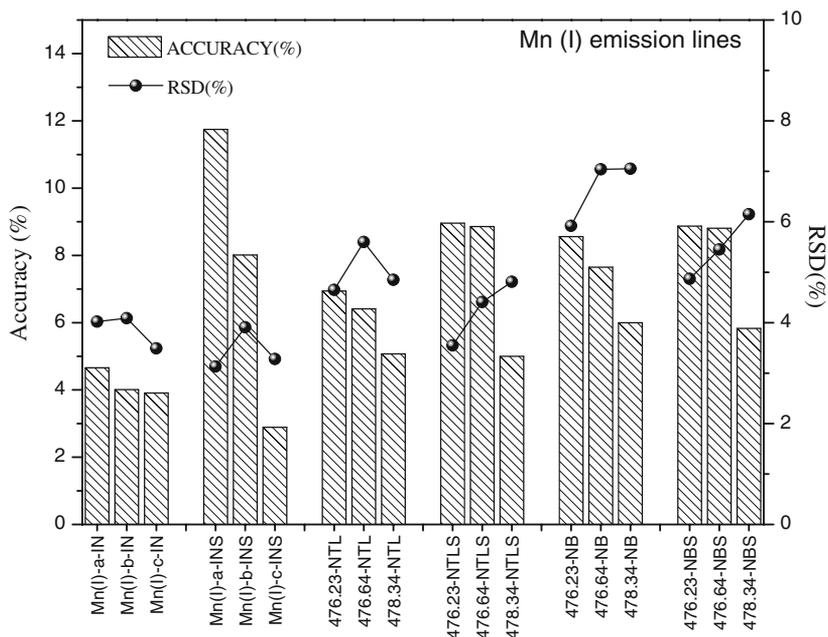
Figure 9. Comparison of average bias and %RSD of selected emission lines of Mn(I) with different normalization models.

half of the area of the peak (spectrally pure side) for analysis which has only three or four pixels. Due to this, the smoothing has arbitrary effect on analytical parameters, as the average of the points inside the peak is more affected by the neighbouring points outside the peak (interference peak). But in non-interference emission line Mn(I) 478.34 nm, the smoothing is effective and shows good analytical results in all the models. The best analytical performance for atomic lines was exhibited by the Mn(I)-c (Mn(I) 478.34 nm/Fe(I) 440.47 nm) with an average bias(%) of ∼2.5% and RSD(%) of ∼3.5% under the INS normalization technique. In the case of ionic lines of Mn, all the emission lines employed were having significant interference. Hence, none of the normalization techniques was able to give promising results. The best results were obtained for Mn(II) 293.44 nm line using NTLS technique having ∼3.8% bias. Similar to Cr, for Ni and Mn, the results obtained using normalized calibration curves are far superior to the results obtained using only raw data.

The results from Cr, Ni and Mn clearly show that the IN or INS method is the best technique among the six techniques considered in this study. The NTL or NTLS technique generates poor analytical values but can be considered as an alternative to IN method where the concentration of the reference element is unknown and variable.

5. Conclusions

Laser-induced breakdown spectroscopy (LIBS) was applied for elemental characterization of high alloy steel using six different normalization techniques with an objective

to evaluate the analytical performance of these techniques. It was found that the accumulation of 60 shots per spectrum gives the best statistically relevant results. Under these optimized conditions, the comparisons of different normalization techniques for steel analysis demonstrates the superiority of IN technique over NTL and NB techniques irrespective of whether it is Cr, Ni or Mn analysis. The smoothing function was also found to produce better analytical results provided the emission lines under study have significant intensity and contain ≥ 7 pixels under the peak. For Cr, Ni and Mn, the best results were obtained with Cr(II) 275.89 nm ($\sim$1.8% bias and RSD(%)), Ni(I) 351.50 nm ($\sim$2% bias and RSD(%)), Mn(I) 478.34 nm ($\sim$3% bias and RSD(%)) by using IN technique. The NTL technique is the second best technique but the analytical performance is good enough to be considered as a viable alternative technique in the absence of IN or where the IN method is not applicable, e.g., where the concentration of the major matrix is unknown. For NTL technique, the best results were obtained using Cr(II) 275.89 nm ($\sim$3% bias and RSD(%)), Ni(II) 241.61 nm ($\sim$3% bias and RSD(%)), Mn(I) 478.34 nm ($\sim$5% bias and RSD(%)) emission lines for Cr, Ni and Mn, respectively.

Acknowledgements

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