

# Accuracy Improvement for Minor Elements Determination Using Modified Self-absorption Correction and One-point Calibration Laser-induced Breakdown Spectroscopy

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**ABSTRACT:** Determination of minor elements is the weakness of one-point calibration laser-induced breakdown spectroscopy (OPC-LIBS), which greatly hinders the further development of OPC-LIBS. The normalization in minor elements determination is seriously influenced by self-absorption effect of matrix element in laser-induced plasma. In this work, a modified self-absorption correction method was proposed in OPC-LIBS. The plasma temperature was determined by the slope of Saha-Boltzmann plots established for minor elements, and the electron number density was calculated from the H $\alpha$  line. The internal reference line of the matrix element was corrected and iterated, until the maximum value of the self-absorption coefficient in the analytical line of minor elements was less than 1. The correction factors were determined based on elemental concentration in the reference sample and Boltzmann plots, and then were used in other samples for elemental determination. Twelve certified 6061 reference aluminum alloy samples and seven micro-alloy steel samples were used as examples for demonstration. Compared with both conventional OPC-LIBS and IRSAC & OPC, the dist in the proposed method (modified IRSAC & OPC) was reduced to 0.537-1.632 wt.% and 0.891-2.805 wt. % for the aluminum alloy and micro-alloy steel, respectively. These results showed that the proposed method can improve the accuracy of detecting minor elements using only one reference sample, which greatly facilitates the application of LIBS.

## INTRODUCTION

Laser-induced breakdown spectroscopy (LIBS) is a promising atomic spectrometry for elemental analysis. As the excitation source in LIBS, a pulsed laser beam is focused onto the sample surface to ablate the sample in interest and generate a plasma. The species and contents of elements are determined by collecting and analysing plasma optical emissions. LIBS has such attractive advantages as minimal sample pre-treatment, simultaneous multi-elemental analyses, non-contact remote detection, fast and in-situ

detection, showing great potential in analyses for biological tissues,<sup>1,2</sup> environmental protection,<sup>3,4</sup> space exploration,<sup>5-7</sup> geological exploration,<sup>8-10</sup> and cultural heritage preservation<sup>11,12</sup>

Generally, the univariate or multivariate regression models are used to establish calibration curves or nonlinear models in LIBS quantitative analysis, where several certified samples with similar matrix are required, and experimental conditions (*e.g.*, laser power density, temperature, humidity) are kept constant during calibration and measurement. However, it is extremely difficult or even impossible to obtain similar reference samples and require

consistency in the experimental conditions. These limitations have hindered the development of LIBS.

Calibration-free laser-induced breakdown spectroscopy (CF-LIBS) considers the matrix as the analytical interest. The elemental concentration information is determined by describing the physical states of the laser-induced plasmas through mathematical models. However, it is hard for plasma to meet the conditions of the several fundamental assumptions in CF-LIBS,<sup>13,14</sup> where the plasma unavoidably suffers from the self-absorption effect.<sup>15,16</sup> The physical mechanism in the experiment is much more complicated than the ideal model. In consequence, the analytical accuracy and precision are unsatisfactory.

In recent years, many researchers have devoted themselves to improving the accuracy of the CF-LIBS analyses. On one hand, the experimental systems were optimized to make plasma closer to the ideal model. Yi *et al.* investigated the effects of laser energy, delay time, and content of elements on the self-absorption effect, the spectra with higher intensity and lower self-absorption were obtained by choosing different locations of collection points.<sup>17</sup> Rezaei *et al.* investigated the effect of different ambient gases on self-absorption at a specific power density, and the results showed that the self-absorption effect was more pronounced in argon than that in helium.<sup>15</sup> Ibanez *et al.* studied the highest intensity of the spectral lines obtained in Ar gas under pressures of 0.1-10 Torr compared to He, and Ne gases.<sup>18</sup> In addition, some unique methods, such as geometrical optical configurations,<sup>19,20</sup> microwave-assisted,<sup>21,22</sup> and stimulated absorption,<sup>22,23</sup> were demonstrated effective in suppressing self-absorption effects and improving the accuracy of quantitative analysis. On the other hand, the theoretical models were modified to describe the plasma more accurately. Yalcin *et al.* proposed to use the Saha-Boltzmann method to calculate plasma temperatures and showed that the temperatures calculated using nitrogen and magnesium emission lines were in agreement.<sup>24</sup> Bulajic *et al.* used the COG model for self-absorption correction and proposed an iterative algorithm to calculate the plasma temperature, electron number density, Gaussian broadening, Lorentzian broadening, and optical path length.<sup>25</sup> Sun *et al.* proposed an internal reference for the self-absorption correction (IRSAC) method, in which an optically thin emission line was selected as an internal reference line for self-absorption correction of other analytical lines.<sup>26</sup> Based on this procedure, Yang *et al.* performed a second correction of the spectral intensity by using electron density and theoretical broadening.<sup>27</sup> Li *et al.* proposed a self-absorption correction method based on blackbody radiation reference.<sup>28</sup> In addition, the columnar density Saha-Boltzmann (CD-SB) plot can be directly used for plasma temperature determination with those strongly self-absorbing resonance lines and strong lines.<sup>29-32</sup> The extended C-sigma approach can address the limitations of the intrinsic constraints of the plasma model and the complexity of the numerical processing caused by the CD-SB plot.<sup>33-35</sup>

Cavalcanti *et al.* proposed a variant of CF-LIBS that requires one certified sample to correct the results of the unknown samples, called one-point calibration (OPC) method.<sup>36</sup> Fu *et al.* analysed three stainless-steel and five heat-resistant steel samples by combining the OPC method with a standard reference line.<sup>37</sup> Borduchi *et al.* used the OPC method on Saha-Boltzmann plots to obtain more accurate plasma temperatures and electron densities by covering a larger energy range.<sup>38</sup> Hai *et al.* used the OPC-LIBS method for the determination of major and miS elements in titanium alloy samples.<sup>39</sup> Hu *et al.* determined Ti, V, and Al in titanium alloys using OPC&SAC.<sup>40</sup> Deng *et al.* utilized OPC&SAC to analyze alloys and ore samples for Cu, Mn, Fe, and Al elements.<sup>41</sup> However, the analytical accuracy of minor element determination is still unsatisfactory in these works, which need a more accurate model to describe. For some minor elements, the fitting accuracy in temperature calculation is further deteriorated due to deficient lines and lower upper-level ranges for establishing a Boltzmann or Saha-Boltzmann plot. Moreover, the matrix elements generally suffer from self-absorption effect, greatly influencing the normalization process in minor element determination.

In our present work, a method of modified self-absorption correction in OPC-LIBS was proposed to improve the determination accuracy of minor elements. The plasma temperature was determined by the slope of Saha-Boltzmann plots established for minor elements, and the electron number density was calculated from the H $\alpha$  line. The internal reference line of the matrix element was corrected and iterated, until the maximum value of the self-absorption coefficient in the analytical line of minor elements was less than 1. The correction factors were determined based on elemental concentration in the reference sample and Boltzmann plots, and then were used in other samples for elemental determination. Aluminum alloy and steel samples were used for demonstration.

## EXPERIMENTAL

**Samples.** The proposed method was validated using twelve certified 6061 reference aluminum alloy samples (NCS Testing Technology Co., Ltd, Chinalco southwest aluminum Co., Ltd, and Northeast Light Alloy Co., Ltd) and seven micro-alloy steel samples (Steel Yanak Testing Technology Co., Ltd), whose elemental information was shown in Tables S1 and S2, respectively. For optimizing spectral SNR (shown in Figs. S1-S4), gate width was 0.5  $\mu$ s, pulse energy was 19 and 35 mJ, and delay time was 1 and 2  $\mu$ s for the aluminum alloy and micro-alloy steel, respectively.

**Experimental setup and process.** The schematic diagram of the experimental instrument used in this work is shown in Fig. 1. A Q-switched Nd: YAG laser (Quantel Q-smart 450, wavelength: 532 nm;

**Fig. 1** Schematic diagram of the experimental setup.

pulse duration: 5 ns; repetition frequency: 10 Hz) was used as the ablation source. The samples were placed on an x-y-z automatically controlled stage, ensuring that a new spot on the sample was ablated each time. The beam was converged to 1 mm below the sample surface by a focusing lens with a focal length of 150 mm, the reason was to avoid breakdown effect upon the sample surface in the air.<sup>42</sup>The experiment was performed in the open air. The plasma emission was collected by an optical fiber and coupled to an echelle spectrometer (LTB, Aryelle 200). The spectrometer was equipped with ICCD (iStarDH-334T, Andor). The optical efficiency of the spectrometer was measured using a radiance-calibrated deuterium-halogen light source (Ocean Optics, DH-2000).

### Theoretical

**CF-LIBS.** Based on local thermal equilibrium (LTE), and optical thinness assumptions, the measured intensity of the emission line can be written as:<sup>43</sup>

$$I_{\lambda}^{ki} = FN_s A_{ki} \frac{g_k}{U_s(T)} e^{-\left(\frac{E_k}{k_B T}\right)} \quad (1)$$

$F$  is the experimental coefficient;  $N_s$  is the number density of the emitting species  $s$ ;  $A_{ki}$  is the spontaneous radiation transition probability;  $g_k$  and  $E_k$  are the degeneracy and energy of upper level  $k$ , respectively;  $k_B$  is the Boltzmann constant;  $U_s(T)$  is the partition function at the temperature  $T$ . Equation (1) can be written as  $y = a * x + b$  to establish a Boltzmann plot, where

$$\begin{cases} y = \ln\left(\frac{I_{\lambda}^{ki}}{A_{ki}g_k}\right) \\ x = E_k \\ b = \ln\left(\frac{FN_s}{U_s(T)}\right) \\ a = -\frac{1}{k_B T} \end{cases} \quad (2)$$

Then the elemental concentration was determined by normalization.

Species in the same ionized state generally have insufficient spectral lines representing the whole energy levels to obtain an

accurate calculated value of plasma temperature. When ion lines from a single ionization of the same element, the Saha-Eggert equation can be used to CF-LIBS. This equation describes the populations of neutral and singly ionic states of the same elements under the LTE condition:<sup>44</sup>

$$\frac{N^{II}}{N^I} = \frac{1}{N_e} \frac{2U^{II}(T)}{U^I(T)} \exp\left(-\frac{E_{ion}}{k_B(T)}\right) \frac{(2\pi m_e k_B T)^{3/2}}{h^3} \quad (3)$$

where  $N^I$  and  $N^{II}$  represent the number density of element  $s$  in the atomic and single ionic states, respectively;  $m_e$  is the electron mass;  $E_{ion}$  is the first ionization energy. Combining Equations (1) and (3), the intensity of the ionic line can be written as:

$$I_{jh}^{II} = FN^I A_{jh}^{II} g_j^{II} \frac{\exp\left(\frac{E_j^{II}}{k_B T}\right)}{U^I(T)} \left(\frac{2(2\pi m_e k_B T)^{3/2}}{N_e h^3}\right) \exp\left(-\frac{E_{ion}}{k_B T}\right) \quad (4)$$

where  $N_e$  is the electron number density, which is generally calculated from the  $H_{\alpha}$  line.<sup>45</sup> Similarly, Equation (4) can be written as  $y^* = m \cdot x^* + q$ , where

$$\begin{cases} y^* = \ln\left(\frac{I_{jh}}{A_{jh}g_j}\right) - \ln\left(\frac{2(2\pi m_e k_B T)^{3/2}}{N_e h^3}\right) \\ x^* = E_{ion} + E_j \\ m = -\frac{1}{k_B T} \\ q = \ln\left(\frac{FN^I}{U_s(T)}\right) \end{cases} \quad (5)$$

According to the classical radiation theories of spontaneous radiation and stimulated absorption, self-absorption is bound to exist, especially at higher elemental content, corresponding to optically thick plasmas. In the next section, a modified self-absorption correction (modified IRSAC) method was proposed to improve the analytical performance of CF-LIBS

**OPC-LIBS.** The slopes of Boltzmann or Saha-Boltzmann plots established for different species in plasma are the same under the LTE condition. It is based on the requirement that the energy transfer process of free electrons to heavy particles via collision transitions must dominate over radiation transitions under high electron number density conditions.<sup>46</sup> Whether the LTE condition is satisfied can be estimated by the McWhirter criterion:<sup>47</sup>

$$N_e > 1.6 \times 10^{12} T^{1/2} (\Delta E_{ki}^s)^3 \quad (6)$$

where  $\Delta E_{ki}^s$  is the energy difference between the level  $k$  and level  $i$ . It is a necessary but not sufficient condition for LTE, because it only applies to homogeneous and static plasmas. It is usually satisfied at the early stages of the plasma evolution when the electron density is of the magnitude of  $10^{17} \sim 10^{18} \text{ cm}^{-3}$ . Once this criterion is fulfilled, CF-LIBS can be applied to the elemental determination.

In CF-LIBS, the content of an element  $s$  can be expressed as

$$C_s = \frac{A_s FN_s}{\sum AFN} \quad (7)$$

where  $A_s$  is the relative atomic mass of element  $s$ ;  $N_s$  is the number density of the element  $s$ , which can be expressed as the sum of the number density of species in the neutral and single ionic states of the same element, *i.e.*,  $(N_s^I + N_s^{II})$ ;  $C_s$  is the content of the element  $s$ .

A sample with certified compositions was selected as a reference sample. The method of modified IRSAC was used only for self-absorption correction of matrix elements, while other species of minor elements did not implement self-absorption correction due to weak self-absorption, too small number of spectral lines, *etc.* After self-absorption correction for its matrix elements, the intercept can be obtained according to the Boltzmann plot. The number densities of minor elements in the reference sample can be expressed as:

$$FN_i = \frac{C_i \sum AFN}{A_i} \quad (8)$$

where  $N_i$  is the total number density of element  $i$  in the reference sample;  $\sum AFN$  was calculated from  $C_i$  and  $A_s FN_s$  according to equation (9), where the number density  $N_s$  was obtained after self-absorption correction of the matrix element.

$$\begin{cases} q_i^I = \ln \left( \frac{FN_i^I}{U_i^I(T)} \right) \\ q_i^{II} = \ln \left( \frac{FN_i^{II}}{U_i^{II}(T)} \right) \end{cases} \quad (9)$$

The modified  $y_i'$  for minor species in the reference sample can be expressed as:

$$\begin{cases} y_i^I = a_s * E_k^I + q_i^I \\ y_i^{II} = a_s * E_j^II + q_i^{II} \end{cases} \quad (10)$$

where  $a_s$  is the average slope of the Saha-Boltzmann plots established for minor elements. Defining the correction factors as:

$$L(\lambda)_i = e^{y_i' - y_i} \quad (11)$$

A correction factor  $L(\lambda)_i$  for each species was applied to other samples for analysis through the equation of  $y' = \ln(L) + y$ .

**The modified IRSAC method.** In the conventional IRSAC, optical thinness in internal reference lines of the matrix element is the fundamental assumption for accurate correcting analytical lines of other elements. Therefore, self-absorption effect in the internal reference line is ignored. Moreover, a spectrometer with high resolution was necessary for accurate profiling the peaks.

However, these conditions are hardly guaranteed. In the modified IRSAC proposed in this work, self-absorption in the internal lines was considered and corrected. The spectral intensity of the internal reference line is expressed as:

$$\hat{I}_{\lambda_R}^{mn} = \frac{I_{\lambda_R}^{mn}}{f_{\lambda_R}} \quad (12)$$

where  $0 < f_{\lambda_R} < 1$ . Furthermore, for determining the self-absorption coefficient, complex iterations are required in the conventional IRSAC to calculate the temperature, whereas the Saha-Boltzmann plots of trace elements were used. Generally, the higher excitation energy of the upper level and lower spontaneous radiation transition probabilities correspond to weaker self-absorption effects. Therefore, the internal reference line can be selected according to the weight of excitation energy and transition probability<sup>48</sup>.

A self-absorption coefficient  $f_{\lambda_R}$  is introduced to describe the spectral emission intensity of the internal reference line, which indicates the degree of self-absorption of the emission lines with values between 0 and 1.  $f_{\lambda_R} = 1$  denotes the line is optically thin, while  $f_{\lambda_R} < 1$  denotes the line becomes optically thick.

$$I_{\lambda_R}^{mn} = f_{\lambda_R} FN_s A_{mn} \frac{g_m}{U_s(T)} e^{-\left(\frac{E_m}{k_B T}\right)} \quad (13)$$

The self-absorption coefficient of the analyzed line can be expressed as:

$$f_{\lambda} = f_{\lambda_R} \frac{I_{ki}^{\lambda} A_{mn} g_m}{I_{mn}^{\lambda_R} A_{ki} g_k} \exp \left( \frac{E_k - E_m}{k_B T} \right) \quad (14)$$

Theoretically,  $0 < f_{\lambda_R} < 1$  when the self-absorption coefficient of the internal reference line is equal to 1. However, uncertainty in the probability of spontaneous radiation transition, measurement errors in the intensity of the emission lines, errors in the relative efficiency correction, background removal misestimation, and the self-absorption effect of the internal reference line, lead to  $f_{\lambda_R} > 1$ . The spectral lines with higher accuracy of spontaneous radiation transition were chosen. Relative efficiency correction and background removal were performed across the entire spectral range. Finally, it was assumed that the self-absorption coefficient of the analyzed lines greater than one was caused by the self-absorption effect of the internal reference line.

At the proper temporal-spatial window, the observation point of plasma is assumed under LTE and spatially homogeneous, meaning that all species have the same temperature. For some elements, such as Fe, Cr, and Mn, even with lower content, numbers of spectral lines were still sufficient for the establishing Saha-Boltzmann plots under optimized conditions. Moreover, the

**Fig. 2** Flow diagram of the proposed method in this work.

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**Fig. 3** LIBS spectra of the aluminum alloy Sample BYG2161X-3# (a) and micro-alloy steel Sample NCS 012010-4 (b).

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Saha-Boltzmann plot mitigates the effect of line strength decline due to self-absorption.

Therefore, the temperatures derived from the fitting slope of these elements were considered as the plasma temperature, due to: (a) slight and ignorable self-absorption effect in these lines; (b) a sufficient number of spectral lines; (c) wider upper-level ranges; (d) parallel lines of minor elements in Saha-Boltzmann plot.

Under fixed temperature deduced by the slope, the self-absorption coefficient of the internal reference line was iterated from 1 to 0 with a step of 0.01, until the maximum value of the self-absorption coefficient of the analysis line was less than 1.  $X$  in Fig. 2 is the maximum value of the self-absorption coefficient of the analytical line. At this point, the self-absorption coefficient of the analytical line was used for its self-absorption correction.

A sample of certified content was used as a reference. Under the

condition of ignorable self-absorption effect in minor elements, only self-absorption in the matrix elements was corrected. Then  $\sum AFN$  was obtained by Equations (2) and (7). With certified elemental contents, total number density, corrected intercept, the correction factors  $L(\lambda)_i$  for each species were obtained. Finally, the correction factors were used in unknown samples for analysis through the equation of  $y' = \ln(L) + y$ . The outline of the proposed method was described in Fig. 2.

## RESULTS AND DISCUSSION

Figure 3 illustrated LIBS spectra of the aluminum alloy (sample BYG2161X-3#) and the micro-alloy steel samples (sample NCS 012010-4). They were selected as the reference samples for establishing analytical models of aluminum alloy and micro-alloy steel, respectively.

**Fig. 4** Saha-Boltzmann plots for the aluminum alloy (a) and micro-alloy steel (b) samples.

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**Fig. 5** Boltzmann plots for the aluminum alloy (a) and micro-alloy steel (b) samples.

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**Fig. 6** Correction factors for each species in the aluminum alloy sample BYG2161X-3 (a) and the micro-alloy steel sample NCS 012010-4 (b).

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Generally, only neutral atoms and single-ionization ions are present in laser-induced plasma.<sup>13,14,26</sup> The NIST database was used to identify emission lines for the analysis of aluminum alloy and micro-alloy steel samples, and the emission lines were listed in **Tables S3** and **S4**, respectively, where the bold fonts represented the internal reference lines. The commonly used four aluminum resonance/intensity lines (Al I, 308.215, 309.271, 394.401,

396.152 nm) in aluminum alloys have severe self-absorption or even self-reversal, and were not retained in this work.

Some lines with large offsets in **Tables S3** and **S4** were removed to optimize fitting ( $R^2 > 0.99$ ) for the established Saha-Boltzmann plot, listed in **Table S5**.

According to Equation (5),  $y^*$  in the ionic lines needs to be subtracted from the logarithmic term containing the unknown temperature. In the iteration procedure, the initial temperature was set to be 10000 K, then the temperature was obtained by optimizing the fitting. The plasma density was calculated from the Stark broadening of the  $H_\alpha$  line, *i.e.*,  $n_e(H_\alpha) = 8.02 \times 10^{12} \left(\frac{\Delta\lambda_{1/2}}{\lambda_{1/2}}\right)^{3/2}$ , their electron number densities were  $1.127 \times 10^{17}$  and  $8.33 \times 10^{16} \text{ cm}^{-3}$  in the plasma of the aluminum alloy and micro-alloy steel samples, respectively. Saha-Boltzmann plots established for the minor elements in the certified samples were shown in **Fig. 4**. The  $R$  squares were all higher than 0.99. The fitting lines were parallel, whose slopes were used to deduce plasma temperatures of 0.93 and 0.88 eV in the aluminum alloy and the micro-alloyed steel, respectively. Based on reasonable assumptions and validation in the literature,<sup>49</sup> different samples of similar substrates have the

same temperature under the same experimental conditions, the temperatures of 0.93 and 0.88 eV deduced by minor elements were applied to other unknown samples.

The correction factors for each species of the reference samples in aluminum alloys and micro-alloy steels were listed in Table S6. Boltzmann plots corrected by self-absorption coefficients (for matrix element) and correction factors (for minor elements) were shown in Fig. 5.

The correction factors  $L(\lambda)_i$  for the emission lines of the aluminum alloy and micro-alloy steel samples were in the vicinity of  $1 \text{ W m}^{-2}$ , as shown in Fig. 6. On one hand, self-absorption effects of matrix element were well corrected by the modified IRSAC method, otherwise, the correction factors of other species derived from the matrix element would certainly deviate far from  $1 \text{ W m}^{-2}$ ; on the other hand, self-absorption of minor elements was ignorable. Some species with correction factors lower than  $1 \text{ W m}^{-2}$  still existed, which might be due to the interference by the emission of other elements (*e.g.*, one element interferes with the emission behavior of another<sup>50</sup>). In addition, the uncertainty of the spontaneous radiation transition probability, and the correction error of the relative efficiency also deviated the intensity of the emission lines from the true value, resulting in  $L(\lambda)_i < 1$ . Attributed to the severe effect of self-absorption, some correction

factors were much higher than  $1 \text{ W m}^{-2}$ , such as Si I, 324.754 nm and Cu I, 324.754 nm spectral lines in aluminum alloys.

For unknown samples, the corrected  $y'$  values were obtained by using the correction factor for each species in the reference sample with the formula of  $y' = \ln(L) + y$  for analysis, Boltzmann plots established by corrected  $y'$  values from aluminum alloy and micro-alloy steel samples were shown in Figs. S5 and S6, respectively.

The criterion of  $\text{dist}^{14,37,51,52}$  was commonly used to overall evaluate the accuracy of all-element determination. The  $\text{dist}$  values of elemental determination for the aluminum alloy and micro-alloy steel were shown in Fig. 7. The detailed results were listed in Tables S7 and S8. Comparing the analytical results of conventional OPC-LIBS, OPC-LIBS with conventional IRSAC, and the proposed OPC-LIBS with modified IRSAC, worse fitting would not absolutely result in low analytical accuracy. For example, the fitting  $R^2$  of Cr II in sample 422e of aluminum alloy was only 0.197, while the predicted content was 0.185 wt.%, very close to the certified value of 0.164 wt.%. Similar results were obtained in the determination of Si, Ti, and Cu in sample NCS 012010-2 of micro-alloy steel. The reason is that small changes in  $y$  values may worsen the fitting under narrower excitation energy levels. The approximate average of their overall

**Fig. 7** Dist values of conventional OPC-LIBS (black scatters and lines), IRSAC&OPC (red scatters and lines), Modified IRSAC&OPC (blue scatters and lines), and the proposed methodology.



determined intercept may have high accuracy. In the same way, a better fitting would not definitely have high analytical accuracy, such as Mn II in sample 422e of aluminum alloy, Mn I and Al I in sample NCS 012010-1 of micro-alloy steel. They are nearly all species with only a single ionization state, use of the Saha equation may lead to inaccessible errors as a consequence of some species do not satisfy the Saha balance. The elements with neutral and single ionization states, wider excitation energy, or higher fitting accuracy in the Boltzmann plot, tend to be highly accurate in determination. For example, Mn and Fe in sample BYG2161X-5#, Fe in sample 424c of aluminum alloy, Cr and Mn in sample NCS 012010-5 of micro-alloy steel. Combined with the proposed self-absorption and OPC (modified IRSAC & OPC), the analytical accuracy was further improved, with dist of 0.537-1.632 wt.% and 0.891-2.805 wt.% for aluminum alloy and micro-alloy steel, respectively. The results with lower dist value can be regarded as high accuracy,<sup>14</sup> especially lots of minor (0.01 wt.% < content < 1 wt.%) or even trace (content < 0.01 wt.%) elements.<sup>53</sup>

For aluminum alloy samples in Fig. 7a, the dist calculated by IRSAC & OPC for some unknown samples was smaller than the proposed method, such as BYG2161X-4#, BYG2161X-5#, 422e, 423d, 6931, and 6934 samples. This can be partly attributed to errors in the evaluation of the matrix elements. For micro-alloy steel samples in Fig. 7a, the dist calculated by IRSAC & OPC and the proposed method were very close due to the self-absorption coefficients obtained by the conventional and modified IRSAC methods were almost the same. In addition, the self-absorption coefficient of the element Si in sample NCS012010-3, for example,

was underestimated, resulting in an assessed content much lower than the true value. In the conventional IRSAC, optical thinness in internal reference lines of the matrix element is the fundamental assumption for accurate correcting analytical lines of other elements, which are hardly guaranteed in most experiments. The reference lines in OPC-LIBS with conventional IRSAC (Figs. 7a and 7b) were selected after a lengthy searching and pre-evaluating processing. Otherwise, the self-absorption in the referenced lines would deteriorate the analytical results, shown in Figs. 7c and 7d. However, for the modified IRSAC method, the self-absorption coefficient of the internal reference line was iterated from 1 to 0 with a step of 0.01, until the maximum value of the self-absorption coefficient of the analysis line was less than 1, meaning that the selection of the internal reference line is free and guarantees the consistency of the analysis results. Detailed results were shown in Tables S7 and S8, Sample BYG 2161X-4# in aluminum alloy and sample NCS 012010-5 in micro-alloy steel were used for comparison. The relative errors range from 6.04 ~ 34.444 % and 3.942 ~ 48.895 % for aluminum alloy and micro-alloy steel, respectively. Corresponding to better results than the conventional OPC-LIBS methods in Table 1.

For those trace elements (content < 0.01 wt.%), the results were still unsatisfactory, although the accuracy was greatly higher than the state-of-the-art works.<sup>31,32</sup> To improve the accuracy of trace element determination, the model still needs to be optimized in the future.

Without considering the stochastic phenomena of laser-induced plasma, the errors of the relative efficiency correction, the uncertainty

**Table 1.** Comparison with relevant methods

Methods <sup>references</sup>	One certified sample	Minor elements (0.01–1 wt.%)	REs (%)	Trace elements (<0.01 wt.%)	REs (%)
<b>CF-LIBS based on Boltzmann plot</b> <sup>43</sup>	Aluminum alloy	Mg, Fe, Mn, Cr, Zn, Ti, Cu	7.7%, 2.2%, 9.1%, 23.1%, 35%, /, /	/	/
<b>CF-LIBS with COG model</b> <sup>25</sup>	Steel (NIST 1172)	Nb	69%	/	/
<b>CF-LIBS based on Saha-Boltzmann plot</b> <sup>13</sup>	Aluminum alloy	Fe, Mg, Cu	9.1%, 13.5%, 72.7%	/	/
<b>SC-LIBS</b> <sup>54</sup>	Bronze (B4)	Ni	84%	/	/
<b>CF-LIBS based on IRSAC</b> <sup>26</sup>	Aluminum alloy	Mn	42%	/	/
<b>Calibration-free inverse method</b> <sup>55,11</sup>	Brooch L	Pb, Zn, Ag	16 %, 22 %, 83%	/	/
<b>OPC-LIBS based on Boltzmann plot</b> <sup>36</sup>	Bronze (162)	Zn, Pb	100%, 30%	/	/
<b>CF-LIBS with IRESIC</b> <sup>56</sup>	Aluminum bronze alloy (4#)	Sn, Si, Ni, Zn, As	/	/	/
<b>OPC-LIBS based on Saha-Boltzmann plot</b> <sup>38</sup>	Sodium chloride	/	/	/	/
<b>CF-LIBS with CD-SRL</b> <sup>31</sup>	Aluminum alloy (5A03)	Si, Mn, Fe, Cu, Zn	41%, 28%, 252%, 1415%, 393%	Ti, Cr, Ni	525%, 873%, 102%
<b>This work (OPC-LIBS with a modified self-absorption correction)</b>	Aluminum alloy (4#)	Si, Fe, Cu, Mg, Mn, Ti	7.1%, 21%, 29.5%, 22 %, 6 %, 15.5%	Cr	34 %
	Micro-alloy steel (5)	Si, Mn, Cr, Ni, Al, Ti, V, Cu	49%, 3.9%, 15.1%, 26 %, 15%, 9.6%, 24 %, 27%	/	/



uncertainty of the spontaneous transition probability, and the self-absorption effects were decreased by using the correction factors. The method of correction factor can partially correct the possible self-absorption effects. For the same species in a reference sample and other unknown samples, the differences in concentration leads to a difference in the degree of self-absorption, but using the correction factor derived from the reference sample for other unknown samples will inevitably lead to a certain amount of error. However, for the trace elements, only a few sparse and faint spectral lines can be observed. The aforementioned factors were difficult to ignore. For instance, the initiation of laser-induced plasmas is a stochastic phenomenon, resulting in plasma temperatures, electron number densities, and plume volumes that were difficult to reproduce precisely. The values of transition probabilities given in different references were different. Measurements from detectors (*e.g.*, radiance calibrated deuterium-halogen sources) yield limited accuracy in terms of spectral efficiency correction. Moreover, the effectiveness of the background removal also affects the spectral intensity.

In OPC-LIBS, elemental determination was based on the optical emission in the ablated plasma plume, which was limited by non-chemometric ablation (*e.g.*, preferential ablation) and the collecting position.<sup>14</sup> The McWhirter criterion was used for LTE verification, but is only a necessary but not sufficient condition. Furthermore, the laser-induced plasma was temporally dynamic and spatially inhomogeneous, LTE condition was hard to satisfy strictly. OPC-LIBS resorts to deducing the total particle density of a given species from the measured Boltzmann distribution at higher energy excitation levels. If the population of ground states was not in equilibrium with the higher states, the total species density was not reflected in the extrapolation results. The correction factors were in the vicinity of  $1 \text{ W m}^{-2}$ , indicating that the self-absorption correction for the matrix elements in this work was reliable. A minor error in the self-absorption correction of matrix elements sets a limit on the accuracy achievable for the minor elements during normalization. Although the determination of the plasma excitation temperature based on minor elements was highly accurate, the plasma might not strictly satisfy the LTE condition, where all species were hard to keep equal in temperature. In addition, plasma was not spatially homogeneous, but the Saha Equation was still used, resulting in an error that cannot be assessed. Optimizing the self-absorption correction model for the internal reference line and extending correction range is probably further improve analytical accuracy, which are our further work.

## CONCLUSION

In this work, determination accuracy of minor elements in OPC-LIBS was improved by using a modified self-absorption

correction method. The matrix elements were corrected for self-absorption, and then the correction factors were determined by the concentration of the elements and the modified Boltzmann plots. Finally, the correction factors were used in unknown samples for analysis. Compared with those in other OPC-LIBS methods, dist values of the proposed method were significantly reduced to 0.537-1.632 wt.% and 0.891-2.805 wt.% for aluminum alloy and micro-alloy steel, respectively. The analytical accuracy for minor element determination was greatly higher than those in the state-of-the-art works on CF-LIBS and OPC-LIBS. Meanwhile, the determination of trace elements was still unsatisfactory, which can be attributed to statistical fluctuations in spontaneous radiative transition probability, correction errors in relative efficiency, negative background removal, non-chemometric ablation, non-uniform plasma, *etc.*, needs a further investigation in the future. In summary, this work proposed a simple and efficient method for the quantitative analysis of minor elements in LIBS application.

## ASSOCIATED CONTENT

Supporting information is available (Fig. S1-S6 & Tables S1-S8).

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## Notes

The authors declare no competing financial interest.

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