Accurate quantitative CF-LIBS analysis of both major and minor elements in alloys via iterative correction of plasma temperature and spectral intensity

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Abstract

The chemical composition of alloys directly determines their mechanical behaviors and application fields. Accurate and rapid analysis of both major and minor elements in alloys plays a key role in metallurgy quality control and material classification processes. A quantitative calibration-free laser-induced breakdown spectroscopy (CF-LIBS) analysis method, which carries out combined correction of plasma temperature and spectral intensity by using a second-order iterative algorithm and two boundary standard samples, is proposed to realize accurate composition measurements. Experimental results show that, compared to conventional CF-LIBS analysis, the relative errors for major elements Cu and Zn and minor element Pb in the copper-lead alloys has been reduced from 12%, 26% and 32% to 1.8%, 2.7% and 13.4%, respectively. The measurement accuracy for all elements has been improved substantially.

Keywords: spectral intensity, plasma temperature, iterative correction, calibration-free laser-induced breakdown spectroscopy (CF-LIBS)

(Some figures may appear in colour only in the online journal)

1. Introduction

Even if small differences in chemical composition of alloys may possibly lead to tremendously different mechanical behaviors and metal grades. Each grade of alloys has its unique application field. Take copper-lead alloy as an example, the low-grade H59 (Cu 57.0%–60.0%, Pb 0.1%–0.5%, and Zn 38.7%–42.1% in weight) exhibits high strength, high hardness, but poor plasticity, and favors hot processing such as hot punching or hot rolling. In contrast, the higher grade H62 (Cu 60.5%–63.5%, Pb 0.08%–0.10%, and Zn 35.75%–38.76% in weight) is good in plasticity, machinability and corrosion resistance, but easy to suffer from dezincification and stress cracking. It is usually used for deep drawing and bending. Therefore, employing an appropriate analytical technique to perform accurate and rapid composition measurement of alloys is of great significance to metallurgy quality control and alloy classification.

Conventional techniques up to now on the alloy composition analysis mainly include photoelectric direct reading spectroscopy, inductively coupled plasma-atomic emission spectroscopy, x-ray fluorescence spectroscopy, and flame atomic absorption spectrometry. However, they are either time-consuming or tedious due to the required complex

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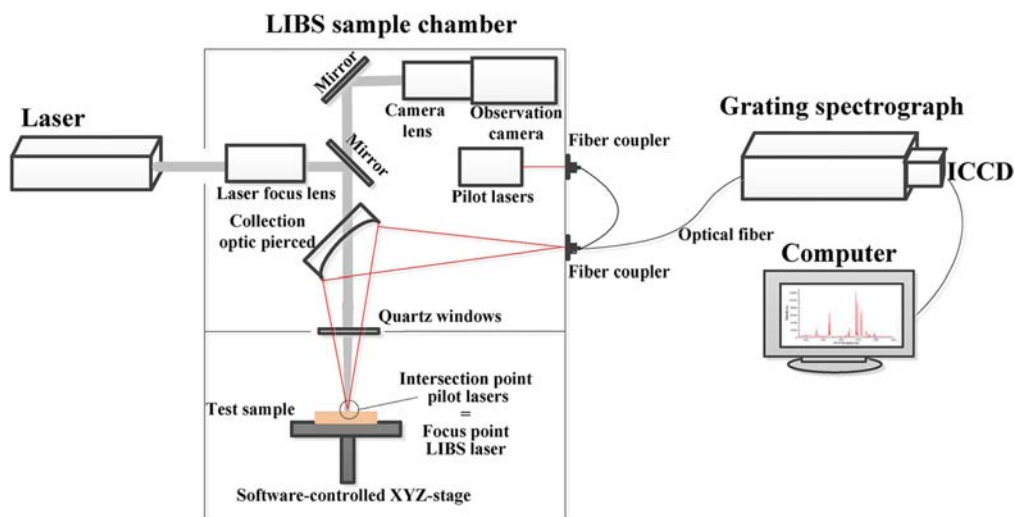[3] Authors to whom any correspondence should be addressed.

Figure 1. Experimental CF-LIBS setup.

pretreatment processes such as crushing, grinding, surface polishing, etc. Laser induced breakdown spectroscopy (LIBS) is nowadays an attractive candidate technique owing to minimal sample preparation, rapid analysis and repeatability [1, 2]. Over the last few years, a large number of reports have demonstrated the potential application of LIBS in this field. For example, Yang *et al* employed 23 standard high-alloy steel samples and relevance vector machine regression to establish the calibration model for quantitative analysis of Cr [3]; Ferreira *et al* made a calibration curve for quantitative analysis of Cu by using 59 soil samples [4]. Although these works have achieved effective quantitative analysis results, it is required to collect or prepare a series of standard samples to establish the calibration model, which greatly limits its potential application.

The classical calibration-free LIBS (CF-LIBS) approach for quantitative analysis of LIBS data was firstly proposed in 1999. It serves as an alternative route to composition measurement where standard samples are not available to make the calibration curve [5–8]. This technology relies on the state of local thermodynamic equilibrium (LTE) in laser-induced plasmas (LIP) and on the knowledge of the values assumed by temperature and electron number density in the acquisition time [9]. Since its first presentation, the approach was verified by several groups on various materials, such as aluminum alloys [6–9], iron alloys [10], copper alloys [11], gold alloys [12], and bronze alloys [13]. For example, Dell'Aglio *et al* employed CF-LIBS to analyze the meteorites, where the plasma temperature was obtained from the emissivity of 25 lines of Fe, and a relative error of 20% was obtained for Co [14]; Burakov *et al* employed CF-LIBS to analyze the copper alloy, where the plasma temperature was obtained from the emissivity of 8 lines of Cu and 4 lines of Pb, and a relative error of 21% was obtained for Pb [15]; Kolmhofer *et al* employed CF-LIBS to analyze the slags, where the plasma temperature was obtained from the emissivity of 13 lines of Ca, 23 lines of Mn, 6 lines of Ti, and the relative errors of Si, Fe, Mn, and Ti were 21%, 32%, 18%, and 23%, respectively [16]. Therefore, although CF-LIBS is capable of performing

quantitative analysis by using the plasma temperature obtained from the Boltzmann plots without standard samples, the typical relative error is on the order of 20%.

It is believed that the measurement accuracy of CF-LIBS is influenced primarily by the following three factors: (1) experimental aberrations, such as intensity fluctuations, inaccurate correction for spectral efficiency of a detection system, etc; (2) inaccurate theoretical parameters for calculations, such as Stark broadening coefficients, partition functions, etc; (3) plasma non-ideality, such as departure from thermal equilibrium, spatial and temporal in heterogeneity, optical thickness, etc [17]. In actual calculation, these factors are usually represented as inaccurate plasma temperature and spectral intensities. To overcome this obstacle, various solutions have been proposed. Gaudiuso *et al* provided an alternative route for plasma temperature determination in CF-LIBS analysis by comparing the elemental composition differences between predictions and standards under different plasma temperature, and a mean relative error of 13.5% was obtained for Sn [18]; El Sherbini *et al* proposed a line intensity correction method by rationing the actual measured line intensity to the intensity expected in absence of self-absorption, and the uncertainties of the integrated intensities were reduced to 10%–20% [19]. Undoubtedly, the CF-LIBS measurement accuracy can be indeed improved by proper correction of plasma temperature or spectral intensity.

In this work, a quantitative CF-LIBS analysis method via iterative correction of plasma temperature and spectral intensity is proposed and expected to realize accurate analysis of major elements Cu and Zn as well as minor element Pb in copper-lead alloys.

2. Experimental

The schematic experimental CF-LIBS setup is shown in figure 1. A Q-switched Nd:YAG pulsed laser (Innolas, SL-100, wavelength: 1064 nm, repetition rate: 10 Hz, pulse energy: 100 mJ) was directed into a sample chamber (LTB,

Table 1. Elemental names and percentage contents of samples used in this work.

Standard	Cu	Pb	Zn	Else
ZBY910	57.09	1.74	41.11	0.06
ZBY902	64.43	1.83	33.45	0.29

Validation	Cu	Pb	Zn	Else
ZBY908B	59.49	1.83	38.60	0.08
ZBY907	59.55	3.06	34.92	2.47

LIPSpector) and focused by an 800 mm focal length focusing lens with the focal point at 2 mm below the sample surface. The spectroscopic emission of the LIP was guided to a grating spectrograph (Princeton Instruments, SP-2750, resolving power: 3100, spectral range: 200–380 nm) that equipped with a time gated ICCD detector (Princeton Instruments, PI-MAX4-1024i) via a 200 μm diameter all-silica optical fiber and the spectra were collected at a delay time of 600 ns and a gate width of 500 ns. Sample mapping was provided by an integrated motorized and software-controlled XYZ-stage and carried out using a grid of analysis spots of 300 μm diameter, spaced at 1 mm intervals. A total of 121 LIBS spectra collected from different positions on each sample surface were averaged to minimize the unintended experimental fluctuations. Additionally, a pilot laser at 635 nm and a real-time video monitoring based on a high-resolution complementary metal oxide semiconductor camera was employed for precise sample positioning and focusing.

Four cylindrical copper-lead alloy samples (38 mm in diameter, 22 mm in height) approved by the China Iron and Steel Research Institute Group were used in this work. A list of the elemental contents (in percentage by weight) of samples is given in table 1. Here, samples ZBY902 and ZBY910 were selected as two boundary standard samples for iterative calculation, while the other two were used for validation purpose.

3. Methodology

The flowchart of the quantitative CF-LIBS analysis methodology via iterative correction on plasma temperature and spectral intensity is illustrated in figure 2, which mainly consists of three steps.

The first step is to determine the variation range of plasma temperature. Two samples, of which the matrix element contents completely cover the variation range of the samples to be measured, should be selected as the boundary standard samples. After obtaining spectra, calculate the corresponding excitation temperature T_i of element i and give a general variation range (T_{min}, T_{max}) of T.

The second step is to find the optimal plasma temperature and the correction coefficient of spectral intensity for the specific minor element. The relative number density of atoms
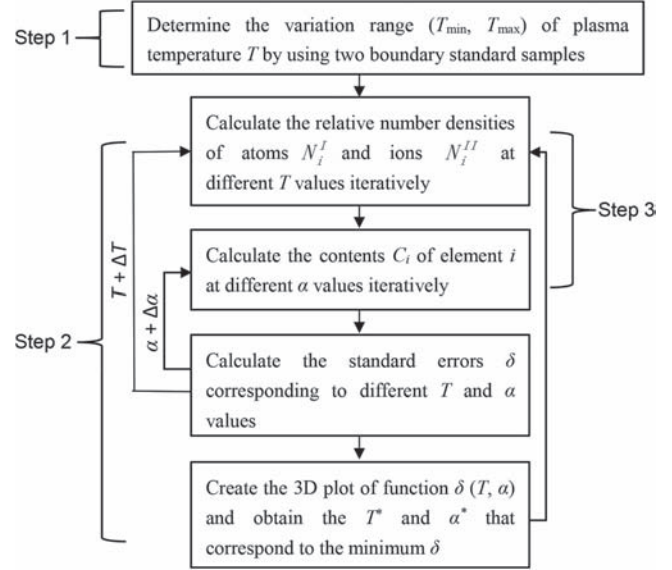
Figure 2. Flowchart of the quantitative CF-LIBS analysis methodology via iterative correction on plasma temperature and spectral intensity.

of element i is given by:

$$N_i^I = \frac{I_i^I Z_i^I}{g_i A_i h v_i} \exp\left(\frac{E_i}{kT}\right),\tag{1}$$

where I_i^I is the integral spectral line intensity, Z_i^I is the partition function, g_i is the degeneracy of the upper level, A_i is the Einstein spontaneous emission coefficient, h is the Planck constant, v_i is the frequency of emission between the upper and lower levels, E_i is the upper energy level, and k is the Boltzmann constant.

The relative number density of ions N_i^{II} of element i is given by:

$$N_i^{II} = 2\frac{N_i^I Z_i^{II}}{N_e Z_i^I}\left(\frac{2\pi m_e kT}{h^2}\right)^{3/2}\exp\left(\frac{E_i}{kT}\right),\tag{2}$$

where Z_i^{II} is the partition function of ions, m_e is the electron mass, and N_e is the electron density.

The mass of element i is given by:

$$M_i = m(N_i^{II} + N_i^I),\tag{3}$$

where m represents the molar mass.

The weight percentage C_i of element i present in the sample is deduced as:

$$C_i = \frac{M_i}{\sum M_i + (\alpha - 1)M_n},\tag{4}$$

where α is a correction coefficient of the specific minor element n.

After calculating the contents of all elements, the standard error δ is evaluated by:

$$\delta = \sqrt{\frac{1}{2}\sum(c_i - c_{i0})^2},\tag{5}$$

where the denominator 2 represents the number of standard samples, c_{i0} is the certified content of element i.

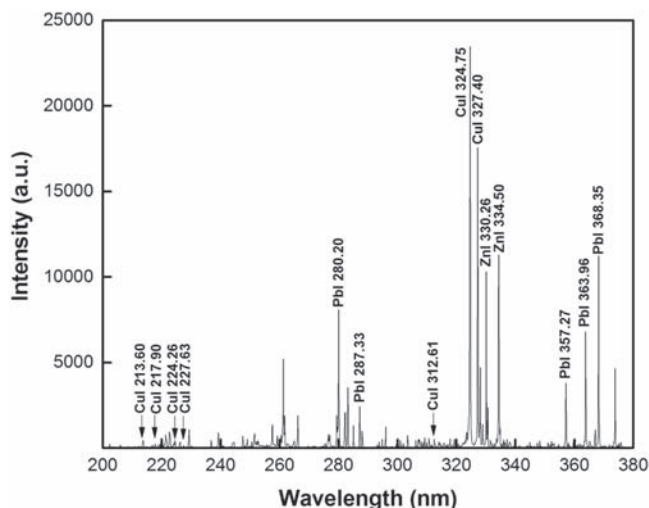**Figure 3.** Typical spectrum recorded for the ZBY902 sample.

Table 2. Wavelengths (λ) and spectroscopic constants (A, E, g) of atomic lines of Cu, Pb, and Zn for confirming T and quantitative analysis.

Species	λ (nm)	A ($\times 10^8$)	E (eV)	g
Cu I	213.60	4.671	8.52	9
	219.23	3.266	8.49	7
	224.26	2.675	8.78	7
	312.61	0.762	8.80	4
	324.75	1.370	3.82	4
	327.40	1.361	3.79	2
Pb I	217.00	1.836	5.71	3
	280.20	1.600	5.74	7
	282.32	0.304	5.71	5
	283.31	0.592	4.38	3
	368.35	1.704	4.33	1
Zn I	330.26	1.070	7.78	5
	334.50	1.500	7.78	7

Figure 4. Comparison of Boltzmann plots of Cu and Pb for samples ZBY910 and ZBY902.

The second-order iterative algorithm in the second step can be described as follows. Firstly, calculate the relative atomic and ionic number densities N_i^{II} and N_i^{I} at different temperatures iteratively according to equations (1) and (2) with a step size of ΔT; secondly, calculate the contents c_i of element i at different correction coefficients α iteratively according to equations (3) and (4) with a step size of $\Delta\alpha$; thirdly, calculate the standard errors δ of all elements corresponding to different T and α values according to equation (5); finally, create the 3D plot of function $\delta(T, \alpha)$ and find the optimal plasma temperature T^* and correction coefficient α^* that correspond to the minimum δ.

The third step is to perform quantitative analysis on unknown samples. The elemental contents in unknown samples can be predicted by substituting the obtained T^* and α^* as well as the plasma spectra in equations (1)–(4).

4. Results and discussion

4.1. Determination of the variation range of plasma temperature

In this study, ZBY910 and ZBY902 were selected as the two boundary standard samples. This is because the contents of the matrix element Cu in them are 57.09% and 64.43%, respectively, which have well covered the variation range of 57.0%–63.5% from low-grade H59 to high-grade H62. A typical spectrum of ZBY902 is shown in figure 3, which reveals all the components Cu, Zn and Pb. Here, 6 Cu I lines and 4 Pb I lines listed in table 2 were chosen to draw the Boltzmann plots for ZBY902 and ZBY910 samples (shown in figure 4) and determine the excitation temperatures of Cu and Pb. Although the points tend to coincide with their corresponding straight fitting lines, the different slopes indicate the different plasma temperatures as well as an apparent violation of the LTE condition. As shown, the variation range of plasma temperature T was determined to be 5000–15 000 K.

4.2. Determination of the optimal plasma temperature and correction coefficient

Taking ZBY902 and ZBY910 as the boundary standard samples, we calculated all the elemental contents and standard errors δ corresponding to different plasma temperatures (5000–15 000 K) and correction coefficients (0–1) iteratively, with step sizes of $\Delta T = 10$ K and $\Delta\alpha = 0.01$. Here, atomic lines Cu I 312.61 nm, Zn I 330.26 nm, and Pb I 280.20 nm were selected as characteristic lines for quantitative analysis due to their relatively small self-absorption coefficients. In this work, spectral intensities of these characteristic lines in the four standard samples were listed as follows: for ZBY910, $I_{Zn} = 17\,232.2$, $I_{Cu} = 1136.78$, $I_{Pb} = 5118.19$; for ZBY902, $I_{Zn} = 6408.78$, $I_{Cu} = 571.14$, $I_{Pb} = 5134.13$; for ZBY908B, $I_{Zn} = 8998.06$, $I_{Cu} = 639.48$, $I_{Pb} = 4998.43$; for ZBY907, $I_{Zn} = 9467.22$, $I_{Cu} = 815.24$, $I_{Pb} = 5772.96$.

In conventional CF-LIBS analysis, the best accuracy is usually obtained for major elements, while for the minor ones
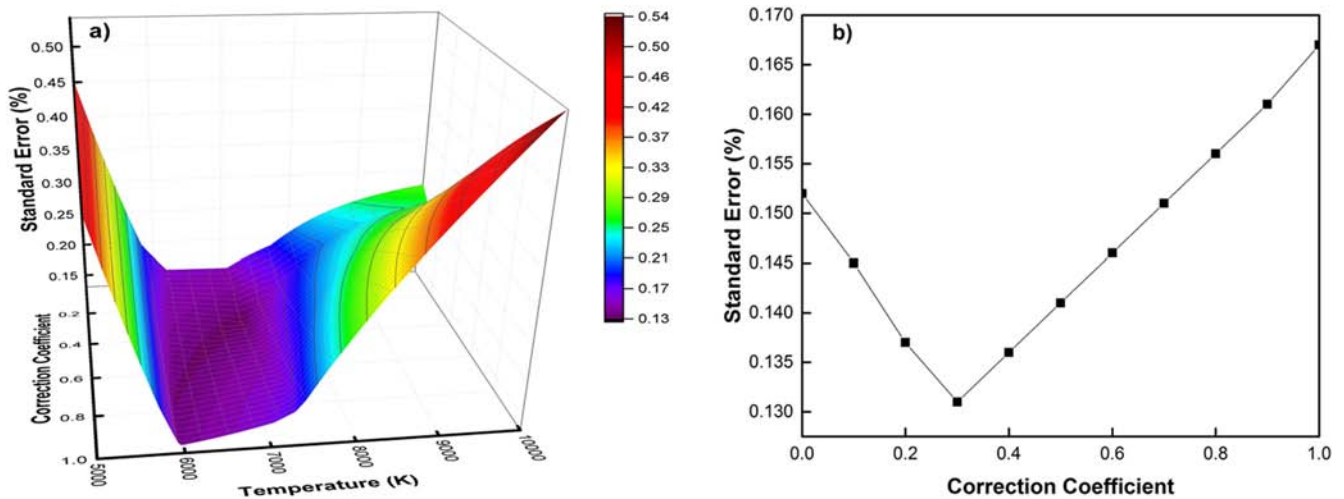
Figure 5. (a) 3D plot of function for the standard samples ZBY910 and ZBY902; (b) the cross section of the 3D plot of $\delta(T, \alpha)$ at $T^* = 7110$ K.

the analysis can only be considered semi-quantitative. This is because of an inhomogeneous distribution of the minor elements in the sample [20]. However, an uncertainty of the order of 1% affecting the major components can correspond to very large uncertainty values on the minor components [17]. Therefore, a correction coefficient α was introduced to calibrate the influence of factors such as spatial inhomogeneity, detection efficiency, self-absorption, spectral line broadening, etc on the spectral intensity, so as to ensure the relative measurement accuracy of minor elements in the sample. Ostensibly, α is a correction to the content of element *n*, but actually it is an amendment to the spectral intensity. In addition to element n, other elements contents can also be corrected to some extent. In general, the coefficient α is approximately equal to the ratio of the certified content of element *n* to the measured content with only correction of the plasma temperature. In our case, the certified and the measured contents of Pb in ZBY902 were 1.83% and 5.99%, respectively, which corresponds to a theoretical α value of approximately 0.31. Thus, the second-order iterative calculation was performed with a wide α range of 0 to 1. The obtained 3D plot of function for the standard samples ZBY910 and ZBY902 are shown in figure 5(a), while the cross section of $\delta(T, \alpha)$ at $T^* = 7110$ K is shown figure 5(b). The optimal plasma temperature T^* and correction coefficient α^* were found to be 7110 K and 0.30, respectively, as the standard error δ reached its minimum of 0.135.

### 4.3. Quantitative analysis on unknown samples

In order to verify the feasibility of the proposed CF-LIBS method, the elemental compositions of the two validation samples were analyzed, with each one being analyzed by 121 successive laser shots for five times. Comparisons of the measured contents and the certified standards are shown in figure 6, where the average relative errors of Cu, Zn and Pb were 1.8%, 2.7% and 13.4%, respectively. In addition to major elements Cu and Zn, but also the measurement error of
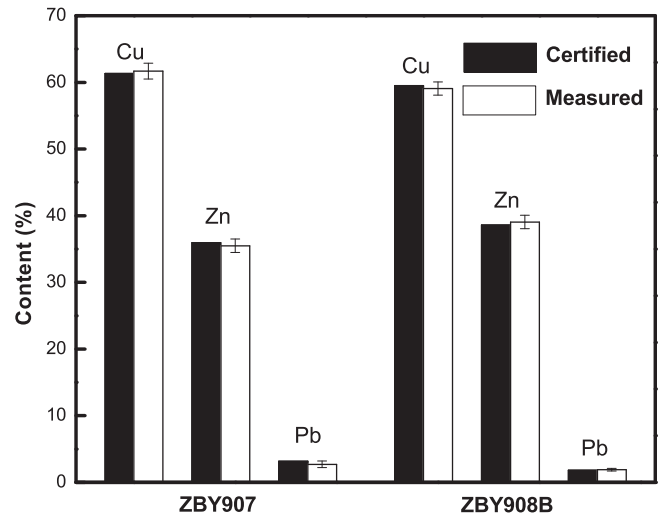
Figure 6. A comparison between the measured contents and the certified standards for Cu, Pb, and Zn through samples ZBY908B and ZBY907. Each sample has been analyzed by 121 successive laser shots for five times.

minor element Pb was relatively small. The good correlation confirms that the proposed method is much suitable for analyzing alloy samples with similar matrices and is able to provide accurate quantitative analysis results on both major and minor elements.

For comparison, the ZBY910 sample was also quantitatively analyzed using the conventional CF-LIBS method, of which the plasma temperature was calculated by averaging plasma temperatures over all the elements. The plasma temperatures calculated from Cu and Pb as well as the average were 9300 K, 6700 K and 8000 K, respectively. The predicted contents of Cu, Zn, Pb under these three plasma temperatures compared to the certified standards are shown in figure 7. As can be seen, the differences in plasma temperature can lead to different measurement errors. Although the average temperature can improve the calculation accuracy to some extent, the
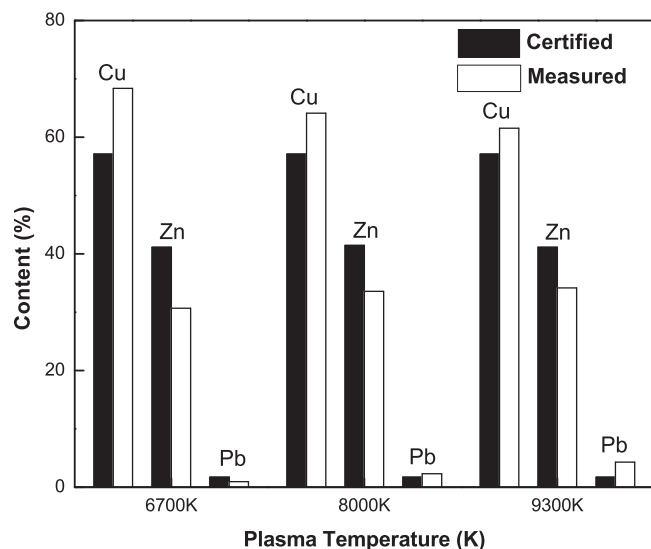
Figure 7. The measured contents for Cu, Pb and Zn of sample ZBY910 at different plasma temperatures using the conventional CF-LIBS method compared to the certified standards.

relative errors of Cu, Zn and Pb still reach 12%, 26% and 32%, respectively, which are obviously much higher than those obtained by the proposed method.

The measurement inaccuracy of the conventional CF-LIBS method was mainly caused by the inaccurate temperature and spectral intensity. For the former, it was attributed to two sides. On the one hand, the CF-LIBS is based on an assumption of LTE, in which case the plasma temperatures for all the sprayed metallic particles in the ablated plume should be the same. However, in practical LIBS experiments, the LIP are in near-LTE conditions, rather than in LTE conditions [21]. This is mainly due to the kinetic ionization recombination processes that caused by the electronic impacts. If the recombination process plays a significant role in the plasma evolution, the Saha balance will be disrupted to non-equilibrium [22, 23]. In addition, the spatial inhomogeneity of plasma can also lead to significant spatial and temporal temperature gradients in its peripheral zones [24]. For the above reasons, we consider the conventional CF-LIBS, which calculates the plasma temperature by averaging the plasma temperatures over several elements, is inaccurate. For spectral intensity, the inaccuracy was caused by self-absorption and spectral line overlapping, which make the measured spectral line wavelength to deviate from the theoretical one and distort the integrated line profile [19].

5. Conclusions

In this study, we propose a quantitative CF-LIBS analysis method via iterative correction on plasma temperature and spectral intensity using two boundary standard samples. By

comparing the standard errors of all the elemental contents through a second-order iterative algorithm, precise plasma temperature and spectral line correction coefficient are determined. Experimental measurement results on copper-lead alloy samples show that, compared to conventional CF-LIBS method, the relative errors of Cu, Zn and Pb have been reduced from 12%, 26% and 32% to 1.8%, 2.7% and 13.4%, respectively. The proposed method has greatly improved the quantitative analysis accuracy of CF-LIBS and realized more accurate measurement of both major and minor elements in alloy samples. It helps to promote the application of CF-LIBS technology in fields such as metallurgy quality control and material classification processes.

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