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Quantitative Analysis of Fe Content in Iron Ore *via* External Calibration in Conjunction with Internal Standardization Method Coupled with LIBS

SHENG Liwen[1], ZHANG Tianlong[1], WANG Kang[2], TANG Hongsheng[1] and LI Hua[1*]

1. Institute of Analytical Science, College of Chemistry & Materials Science, Northwest University,
Xi'an 710069, P. R. China;
2. College of Science, Chang'an University, Xi'an 710064, P. R. China

Abstract The external calibration in conjunction with internal standardization(ECIS) coupled with laser-induced breakdown spectroscopic(LIBS) technique was proposed to perform the quantitative analysis of Fe content in iron ore. The plasma temperature and the electron number density were calculated to prove that the plasma was under local thermodynamic equilibrium(LTE) conditions and to ensure that the integral intensities of Fe I lines were reasonable. In addition, the result of the quantitative analysis shows a content of (20.26±0.59)% by mass of Fe in the iron ore. It was determined by four calibration curves, drawn for four emission lines of Fe I(373.48, 373.71, 404.58 and 438.35 nm) normalized by Mn I line, base on the ECIS method which can eliminate the influence of matrix effect and improve the accuracy of quantitative analysis, compared with the standard addition method. Both the results of these two analytical methods were compared with that listed in the Standard Substance Certificate. The percentage content of Fe in the same sample of iron ore by the ECIS method was (20.17±0.08)% by mass, which shows a good performance to analyze the Fe content of iron ore in combination with LIBS.

Keywords Laser-induced breakdown spectroscopy(LIBS); External calibration in conjunction with internal standardization(ECIS) method; Chemical analysis; Iron ore

1 Introduction

Iron ores are rocks and minerals from which metallic iron can be economically extracted. For iron ore analysis, traditionally high precision multi-element analysis has been performed *via* traditional techniques, such as X-ray fluorescence(XRF)[1] and X-ray diffraction(XRD)[2,3]. However, the method mentioned above would cost much time to pre-treat samples. In addition, since the reagent of strong acid and heavy metal ions are in the solution, they would pollute the environment.

Laser-induced breakdown spectroscopy(LIBS) has been an analytical technique over the past three decades, which can determine the element composition of gases, liquids, solids based on the radiation emitted by laser-induced plasma(LIP). LIBS has various advantages, such as minimal or no sample preparation, rapid multi-component analysis, the capacity for remote analysis, and the ability to analyze almost any types of materials, *e. g.*, cultural heritage[4], as well as industrial analysis[5,6], environmental monitoring[7,8], security and forensic analysis[9], biomedical analysis[10,11], space exploration[12], and mineral analysis[13—16], particularly, iron ore analysis. Grant *et al.*[17] reported both the qualitative and semi-quantitative multi-element analysis of iron ore by LIBS, which, however, couldn't achieve high precision(the precision ranges from *ca.* 2% to *ca.* 25%).

One of the main difficulties for a precise and accurate quantitative analysis by LIBS is matrix effects which could influence spectral intensity and lead to the inaccurate quantitative analysis[18]. The external calibration in conjunction with internal standardization(ECIS) was used to eliminate the influence of matrix effect and improve the accuracy of quantitative analysis. Herein, using standard addition method is to produce the external calibration effect which could eliminate the influence of matrix effect[19], meanwhile internal standardization is to calibrate the integral intensities of analytical lines of the sample[20]. So, in order to achieve high accuracy and precision, we utilized the ECIS method coupled with LIBS to quantitative analyze the Fe content of iron ore.

In the present work, local thermodynamic equilibrium(LTE) was judged by calculating the plasma temperature and electron number density of Fe[21]. In addition, the Fe content of iron ore was determined by the four calibration curves, drawn for four emission lines of Fe I(373.48, 373.71, 404.58 and 438.35 nm) normalized by Mn I line, based on the ECIS method which can eliminate the influence of matrix effect and improve the accuracy of quantitative analysis, compared with

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*Corresponding author. E-mail: huali@nwu.edu.cn

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the standard addition method.

2 Experimental

2.1 LIBS Spectrometer

The experimental configuration used in this work is schematized in Fig.1. A Q-switched Nd:YAG laser(LOTIS, TII 2131, Belarus) operated at 1064 nm(pulse duration of 10 ns) with a maximal output pulse energy of 83 mJ and repetition rate of 5 Hz was used to irradiate the samples. The Nd:YAG laser beam was focused onto the target surface by a 50 mm focal length plano-convex lens at 90° angle and the optical fiber was positioned at a distance of about 20 mm from the surface of the sample, making an angle 45° to the laser beam. The samples were placed directly on an *x*-*y*-*z* manual micrometric stage. The distance between the lens and the sample surface was set to approximately 50 mm to insure reproducible breakdown and produce an almost hemispherical plasma plume. The plasma plume focused into an optical fiber(with a 1000 nm core diameter and 0.22 numerical aperture) coupled with the entrance of an Echelle spectrometer(ARYELLE-Butterfly, LTB400, Germany). The spectrometer provides a constant spectral resolution(CSR) of 6000 over a wavelength range of 220—800 nm displayable in a single spectrum. An electron-multiplying charge-coupled device(EMCCD) camera (QImaging, UV enhanced, 1004×1002 Pixels, USA) combined with the spectrometer was used for detection of the dispersed light. To prevent the EMCCD from detecting the early plasma continuum, a mechanical chopper was used in front of the entrance slit. All spectra were acquired after a 3.0 μs delay from the laser pulse.

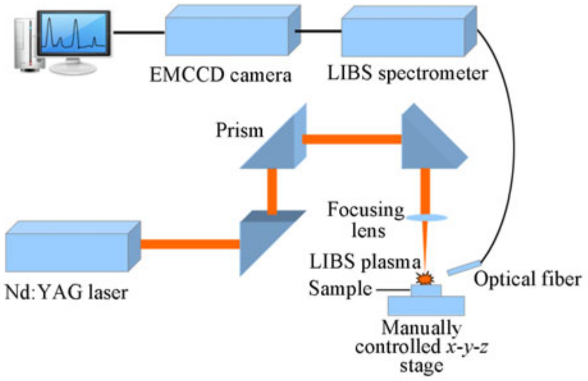

Fig.1 LIBS experimental configuration for iron ore analysis

2.2 Sample Processing

This study was performed on a standard iron ore sample(GBW07822) from the Institute of Geophysical and Geochemical Exploration(China). Before obtaining the LIBS spectra, the iron ore samples were pre-treated. According to the Fe content[(20.17±0.08)%] of the iron ore in Standard Substance Certificate, we settled the order of magnitudes of successive additions which was similar to that of known concentration, applied to the external calibration. Then 5 samples respectively containing 0, 10%, 20%, 30% and 40%(mass fraction) of added Fe_2O_3 were prepared, by mixing in appropriate proportions with the iron ore samples. To eliminate the matrix effect of the sample or at least reduce this effect to a minimum, it is significant to make the distribution of all the elements homogeneous in the subsequent LIBS experiments. The polyethylene was used to collect the powdered sample, which was compressed to form a pellet by a manual pellet presser with sufficient pressure(20 MPa) lasting for 2 min. To obtain the reasonable spectral intensity of each pellet sample, 15 spectra were obtained at different positions of each pellet, and then the respective average intensity was calculated from 15 spectral intensities. A measured spectrum was collected as an accumulation of 20 laser shots per location for the purpose of improving the signal-to-noise ratio.

3 Results and Discussion

3.1 Plasma Characterization

The wavelength region of the spectrum(373.00—440.00 nm) of the pure iron ore is shown in Fig.2, in which the region consists of various Fe spectral lines. The laser-induced plasma generated on iron ore pellet sample surface is characterized through its plasma temperature and electron number density under LTE conditions. According to the Boltzmann plot method with Fe spectral lines, the various Fe spectral lines whose information is shown in Table 1 were used to build a good linear fitting straight line, and the laser-induced plasma temperature was determined then. These lines are isolated and free from interferences of other elements.

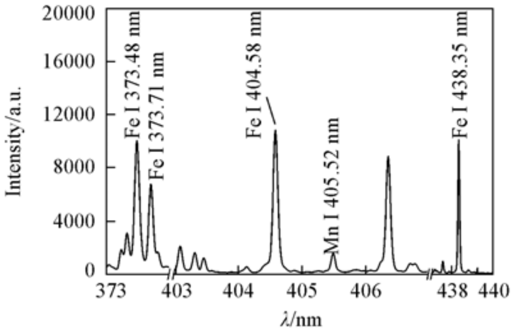

Fig.2 LIBS spectrum of pure iron ore ranging of 373.00—440.00 nm

The major identified lines are shown, such as Fe I(373.48, 373.71, 404.58 and 438.35 nm) and Mn I(405.52 nm).

If the plasma is under LTE conditions, its temperature(T) can be obtained from the spectral line integral intensity because the population distribution is a function of T according to Boltzmann equation[22]. To calculate plasma temperature, the parameters of spectral lines from NIST dataset are shown in Table 1. Boltzmann plots of Fe spectral lines from pure iron ore are shown in Fig.3.

Then, because the full width half maximum(FWHM) of spectral line is the function of plasma electron number density, plasma electron number density can be calculated *via* experimental Stark broadening[23]. As can be seen, Lorentzian profile of Fe I line(438.35nm) obtained from pure iron ore sample is shown in Fig.4, whereas those containing 0, 20.0%, 30.0%, 40.0% added Fe_2O_3(A. R. grade) are shown in the inset. It is obvious that the intensities of Fe I lines(438.35 nm) of 4 samples present linear increased tendency with added Fe_2O_3(A. R. grade) in concentration gradient.

Table 1 Fe spectral lines from pure iron ore used for Boltzmann plot*

λ/nm	I_λ^{ki} /a.u.	$10^{-8}A_{ki}$/s^{-1}	E_{ki}/eV	J
278.81	1110.496	0.590	5.32	6
344.06	3289.024	0.171	3.61	3
358.12	5578.330	1.02	4.33	6
371.99	4301.314	0.162	3.34	5
373.48	7086.332	0.902	4.19	5
373.71	4999.526	0.141	3.38	4
374.56	4699.506	0.115	3.40	3
374.95	5246.718	0.764	4.23	4
385.99	4945.106	0.0969	3.22	4
388.63	1818.372	0.0530	3.25	3
404.58	7043.650	0.863	4.56	4
438.35	6929.068	0.500	4.32	5
258.59	2541.090	0.861	4.81	3.5
259.84	1738.780	1.42	4.83	2.5
260.71	2537.694	1.74	4.85	1.5
261.19	2856.680	1.23	4.93	3.5
273.95	3185.844	1.90	5.52	3.5
274.93	1999.046	2.10	5.56	3.5
275.57	2768.326	2.10	5.50	4.5

* λ is the wavelength of an atomic or ionic species; I_λ^{ki} is the intensity of emission line; A_{ki} is the transition probability for the given line; E_{ki} is the energy of upper energy level; J is the degeneracy.

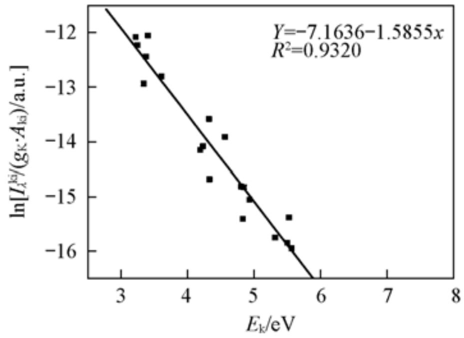

Fig.3 Boltzmann plot of Fe spectral lines from pure iron ore

g_k(dimensionless) is the statistical weight. The plasma temperature is 7312.65 K.

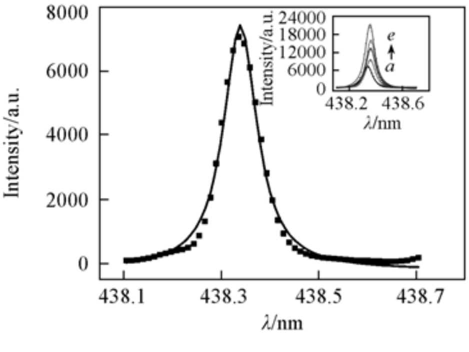

Fig.4 Lorentzian profile of Fe I line(438.35 nm) obtained from pure iron ore

The FWHM is 0.0836. The inset shows Lorentzian profiles of Fe I lines(438.35 nm) obtained from iron ore samples containing 0(*a*), 10.0%(*b*), 20.0%(*c*), 30.0%(*d*), 40.0%(*e*)(mass fraction) added Fe_2O_3, respectively.

Herein, we used Lorentzian profiles of Fe I lines(438.35 nm) of 4 samples from pure iron ore to calculate the electron number density. The lower limit of the electron number density where the plasma is under LTE conditions is calculated through[24]

$$N_e \geqslant 1.4\times10^{14}T^{1/2}(\Delta E)^3 \qquad (1)$$

where N_e is the electron number density, T the plasma temperature, and ΔE the energy difference between upper energy and lower energy[25]. The parameters of LTE in the pure iron ore are shown in Table 2.

Table 2 Parameters of LTE in pure iron ore

w(Added Fe)(%)	T/K	ΔE/eV	N_e/cm^{-3}	M^*/cm^{-3}
0	7312.65	1.35	2.97×10^{16}	3.09×10^{15}

* M(experimentally calculated density)=$1.4\times10^{14}T^{1/2}(\Delta E)^3$.

The result above mentioned meets Eq.(1) from the calculation of electron number density and plasma temperature. In the present case, for Fe I at 438.35 nm, the experimentally calculated density(M) is less than the lower limit value of electron number density(N_e), verifying that the laser-induced plasma is under LTE conditions. So, as the plasma is under LTE conditions, the intensities of Fe I lines(373.48, 373.71, 404.58 and 438.35 nm) can be used to quantitatively analyze the Fe content of the iron ore.

3.2 Quantitative Analysis

Since utilizing the accurate intensities of Fe I lines for analysis, the internal standardization can calibrate the spectral intensities of Fe I lines and increase the coefficient of linear fitting by the internal standard line. Because Mn I line in the same spectral window(373.00—440.00 nm) fulfills the conditions[26]: (1) it is reasonably strong and isolated to avoid interference with other spectral lines; (2) it has similar energy difference(ΔE=1.33 eV) with those of Fe I analytical lines; (3) it is simultaneously detected in a single laser shot to avoid complexities in line. Herein, the spectral lines of Fe and Mn in the iron ore were identified *via* NIST database[25], especially, the Fe I lines at wavelength 373.48, 373.71, 404.58 and 438.35 nm, respectively. The Mn I line was chosen as an internal standard line at wavelength 405.52 nm. For each spectrum of the samples with different added concentrations of Fe_2O_3, the intensities of the Fe I lines were just normalized with Mn I line intensity. A calibration curve that the intensity of Fe I line normalized with Mn I line *vs*. the concentration of added Fe in percentage was plotted. Owing to the Fe presented in the original sample, the y-axis is non-zero intercept; therefore the intercept on the negative x-axis shows the inherent concentration of Fe in the sample. Such four calibration curves were drawn for the four emission lines of Fe I in the wavelength region which contains both Fe I and Mn I spectral lines, through the intercept method[20]. From Fig.5, it shows the extrapolated calibration curves of the intensities of four emission lines of Fe I normalized with Mn I line(405.52 nm) *vs*. concentration(mass fraction) of added Fe. The calibration curves of the Fe element in iron ore samples show a good linear fit(R^2>0.9) within the experimental uncertainty. The average value of four values is shown in Table 3.

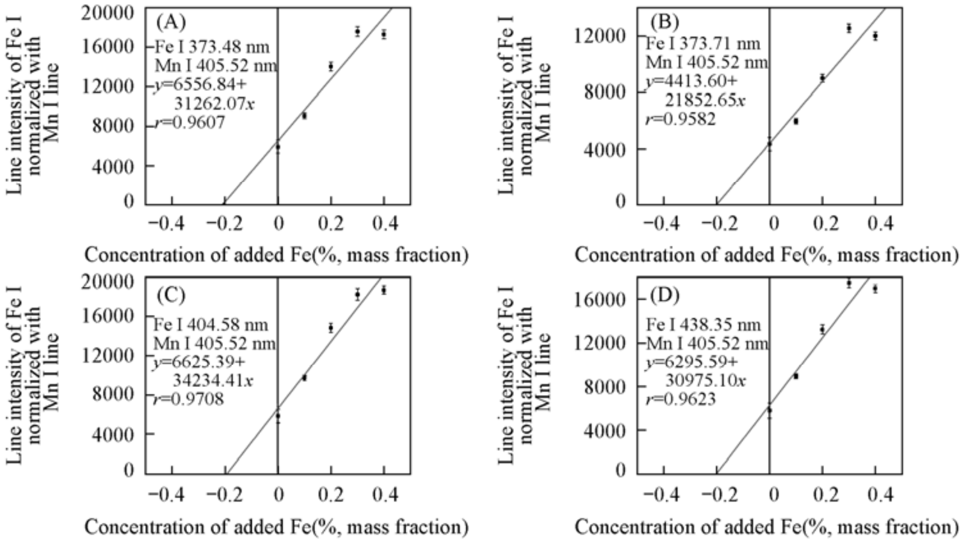

Fig.5 **Extrapolated calibration curves of the intensity of four emission lines of Fe I normalized with Mn I line(405.52 nm) *vs*. concentration of added Fe(mass fraction), for emission lines at 373.48(A), 373.71(B), 404.58(C) and 438.35 nm(D) *via* ECIS method**

Table 3 Content of Fe in iron ore *via* ECIS method

Fe I line wavelength/ nm	r	Slope of the fitted line	Mass fraction of Fe(%)	Mean w(Fe) (%)	Relative tolerance (%)
373.48	0.9607	31262.06	20.97	20.26	0.4462
373.71	0.9582	21852.65	20.20		
404.58	0.9708	34234.41	19.53		
438.35	0.9623	30975.10	20.32		

3.3 Comparison with Standard Addition Method

Standard addition methods[27] are particular useful for analyzing complex samples in which the likelihood of matrix effect is substantial. One of the most common standard addition procedures involves adding one or more increments of a standard analyte to sample containing identical volumes. As usual, the signal is plotted on the y-axis; in this case the x-axis is graduated in terms of the amounts of analyte added. The regression line is calculated in the normal way, while space is provided for it to be extrapolated to the point on the x-axis at which y=0. This negative intercept on the x-axis corresponds to the amount of the analyte in the test sample[23].

Herein, standard addition method was compared with ECIS method, which used the integral intensity of Fe I lines without normalization. As can be seen, standard addition plots are shown in Fig.6.

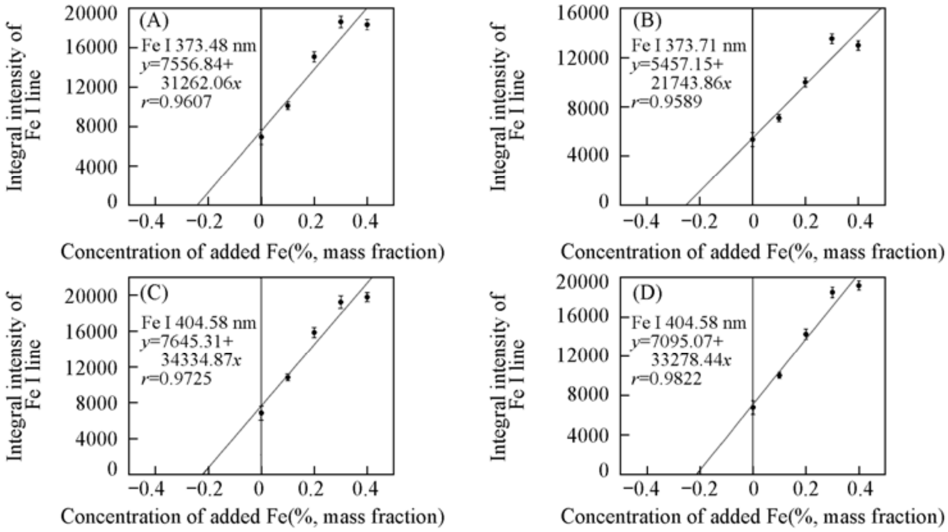

Fig.6 **Extrapolated calibration curves of the intensity of four emission lines of Fe I *vs*. concentration of added Fe (mass fraction) using standard addition method, for emission lines at 373.48(A), 373.71(B), 404.58(C) and 438.35 nm(D)**

Table 4 shows the Fe content of iron ore is 23.22%, standard deviation of 15.12%, *via* standard addition method. Compared with standard addition method, ECIS method shows a good performance to analyze the Fe content of the iron ore combined with LIBS. The determination of Fe content in the iron ore is summarized in Table 3 using the four Fe I emission lines. It shows that the average of four values as the determination of Fe content in the iron ore is (20.26±0.59)% compared with the value of Standard Substance Certificate [(20.17±0.08)%] by volumetric analysis. The absolute error is

(0.09±0.51)% and the relative tolerance is 0.4462%.

Table 4 Content of Fe in iron ore *via* standard addition method

Fe I line wavelength/ nm	*r*	Slope of the fitted line	Mass fraction of Fe(%)	Mean *w*(Fe) (%)	Relative tolerance (%)
373.48	0.9607	31262.06	24.17	23.22	15.12
373.71	0.9589	21743.68	25.10		
404.58	0.9725	34334.87	22.27		
438.35	0.9822	33278.44	21.32		

3.4 Calculation of LOD

Besides, the limit of detection is usually defined as the concentration that originates a net line-intensity equivalent to three times the standard deviation of the background[28]. The LOD for each element based on different analysis lines was calculated according to the IUPAC definition:

$$\mathrm{LOD} = 3\sigma/s \qquad (2)$$

where σ is the standard deviation of the background, and S is the sensitivity given by the slope of the corresponding calibration curve. In our work, σ was determined from 20 measurements of the background signals under the same experimental conditions, where the background signal was the baseline of characteristic peak. Table 5 lists the slopes, σ values, and LODs determined in this work.

Table 5 Limits of detection for different elemental spectral lines

Element	Slope	3σ	LOD
Fe I 373.48 nm	31262.06	986.57	0.031558
Fe I 373.71 nm	21852.65	945.72	0.043277
Fe I 404.58 nm	34234.41	851.23	0.024865
Fe I 438.35 nm	30975.10	865.39	0.027938

4 Conclusions

The present work reveals that the ECIS method combined with LIBS shows pretty good result on the detection of Fe content in GBW07822 iron ore. LTE was judged by calculating the plasma temperature and electron number density of Fe before the quantitative analysis of the Fe content in iron ore. Then, the quantitative analysis of Fe content in iron ore is to build the calibration curve of normalized integral intensity of Fe I lines by Mn I line *vs*. the added concentration of the analyte element(Fe) by mass. The result shows a content of (20.26±0.59)% by mass of Fe in the iron ore based on four emission lines of Fe I(373.48, 373.71, 404.58 and 438.35 nm) and Mn I lines as internal standard line, by the ECIS method coupled with LIBS compared with the standard addition method. Both the results of these two analytical methods were compared with the Standard Substance Certificate. The mass fraction of Fe in the same sample of iron ore *via* the ECIS method was (20.17±0.08)% according to Standard Substance Certificate, with an absolute error of (0.09±0.51)%, and a relative tolerance of 0.4462%. ECIS method combined with LIBS shows a good performance to analyze the Fe content of iron ore. Through the ECIS method combined with LIBS, we can analyze the raw iron ore and guide quality assurance and control in iron and steel industry.

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