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Quantitative analysis of phosphorus in steel using laser-induced breakdown spectroscopy in air atmosphere

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Quantitative analysis of phosphorus in iron/steel in air atmosphere is considered a challenge for laser-induced breakdown spectroscopy (LIBS) due to strong interference from the matrix. In this study, the interferences from iron and copper lines to the P I 214.91 nm line on different gate delays were studied. The interference to the P I 214.91 nm is mainly from the ionic lines of iron and copper in the steel. By choosing the gate delays carefully, the interference can be reduced. Requirements for the detection of P I 214.91 nm in steel plasma on the spectral resolution and sensitivity of spectrometer were also studied. Based on the results, a Czerny-Turner spectrometer equipped with an ICCD camera with a minimum spectral resolution of 0.03 nm is suggested for this application. Finally, successful quantitative analysis of phosphorus in the UV-VIS spectral range was carried both on pig iron and low alloy steel. For the pig iron, the R-squared (R^2) factor of calibration was 0.9992, the limit-of-detection (LoD) was 12 ppm and the background equivalent concentrations (BEC) was 0.11 wt.%. For the low alloy steel, the R^2 factor of calibration was 0.995, the LoD was 9 ppm and the BEC was 0.05 wt.%. The interference of copper lines to P I 214.91 nm was not observed. The results have shown that accurate quantitative analyses of phosphorus in iron/low alloy steel in open air using a simple LIBS setup are possible.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) has been proven to be a versatile analytical technique during the past decades. LIBS has many advantages,[1-5] such as the ability of detecting nearly all elements in any physical form (liquid, solid, gas, etc.), rapid and simultaneous multi-element detection, no or simple sample preparation, nearly non-destructive, capability of in-situ and real-time analysis,[6-8] field deployment, and remote analysis for military[9-11] and space applications.[12] Application of LIBS to steel industry including iron (Fe) ore selection,[13, 14] process control,[15, 16] and iron slag analysis[17] has been studied widely by many groups. Several review works[15, 18, 19] have already been present.

As it is well known, careful content control of light elements such as phosphorus (P) and sulfur (S) is critical for the quality assurance of steel products. Based on the national standards of China, content of P in pig iron should be lower than 2.5% (No. GB/T 20932-2007), and content of P in low alloy steel should be lower than 0.035% (No. GB/T 1591-2008). Detection of P in steel using LIBS in vacuum ultraviolet (VUV) spectral range using P I 177.50 nm or 178.28 nm line has been studied by many groups. Some of the works have been summarized in Table 1. Generally, the limit of detection (LoD) of P in steel is down to 4 ppm,[20] the R-squared (R^2) factor of calibration is up to 0.998,[21] and the background equivalent concentration (BEC) is down to 0.013%.[22] However, as the P I 177.50 and 178.28 nm lines are in the VUV spectral range, their detection requires vacuum or purged inert gases for the spectrometer system and the light collection pathway. This requirement imposes challenges in many applications in steel industry, and hence detection in open air is still needed.

To detect P in steel in open air, X. K. Shen *et al.*[23] has combined LIBS with laser-induced fluorescence (LIF). A wavelength-tunable optical parametric oscillator (OPO) laser was tuned at 253.56 nm to selectively excite P in steel plasmas at a delay time of 8 µs. A LoD of 0.7 ppm was realized using the P I 213.62 nm line. Nearly at the same time, detection of P using LIBS-LIF was also studied by H. Kondo *et al.*[24] The probe laser was tuned to 255.49 nm. Fluorescence line at P I 214.91 nm is free from interference from the iron matrix, has a good linear correlation with P contents in steel samples, and has a LoD of about 5.4 ppm. However, utilization of wavelength-tunable laser is expensive and complex for many applications.

Recently, H. Heilbrunner *et al.*[25] used collinear double-pulse LIBS to analyse trace elements including P in sintered iron oxide in air, and compared the performances of charge coupled device (CCD) and intensified charge coupled device (ICCD) detectors. The CCD detector was considered providing considerable higher signal-to-noise ratios (SNR) and/or better LoDs than that of ICCD. The LoD for P was about 10.3 ppm with the CCD camera and 30.7 ppm with the ICCD camera. As the matrix of the sintered iron oxide is significantly different from that of the iron and steel, it is still not a success for quantitative analysis in open

Table 1 LIBS characterization of phosphorus in various steel matrices.

Matrix	Exciting mode	Analytical line (*nm*)	LoD (*ppm*)	R^2	Content Range (*ppm*)	Ref. no.
Steel	Triple pulses (amount to 300 mJ)	178.28	9	0.998	0 - 600	21
Steel	Single pulse (60 mJ)	178.28	6	≥ 0.99	About 2 - 120	22
Liquid steel	Double pulses (amount to 300 mJ)	178.28	21	/	/	15
Liquid steel	Triple pulses (amount to 120 mJ)	178.28	21	0.99	60–890	16
Low alloy steel	Micro-analysis	177.50	36	0.96	About 80 - 430	26
Low alloy steel	Double pulses (amount to 400 mJ)	178.28	4	0.99	5 - 600	20

air of P in steel using LIBS alone.

Because of its significance and potential in steel industry, quantitative analysis of P in pig iron and low alloy steel was carried out in UV-VIS spectral range using a simple LIBS setup. Qualitative analysis was carried out for the pig iron at first, and the main lines of P in the UV-VIS range were compared to find the best analytical line. Interference from iron and copper (Cu) to the P I 214.91 nm were studied using pure reference materials and the pig iron samples. Requirements of the spectral resolution and sensitivity of the spectrometer were also studied for P detection. After that, quantitative analysis was carried out for pig iron and low alloy steel using P I 214.91 nm.

2. Experimental

The experiment setup for the LIBS is schematically shown in Fig. 1. The plasma was generated by a Q-switched Nd:YAG laser (Beamtech, Nimma-400, pulse duration of 8 ns) operating at 532 nm and 3 Hz. The laser beam was focused onto the target at the normal incidence by a plano-convex lens (f = 150 mm) with a focal point of 5 mm below the target surface. A pulse energy of 60 mJ was used in this study, corresponding to a laser fluence of 30.6 J/cm^2. The target was mounted onto a motorized X-Y translation stage equipped with a manual Z axis translation stage for precise adjustment of the target height. The light from the laser-induced plasma was collected using a UV-NIR light collector (Andor, ME-OPT-0007), coupled to a spectrometer through a fiber. A Czerny-Turner spectrometer (Princeton Instruments, Isoplane SCT320) having three gratings (3600, 2400, and 1200 lines/mm) and equipped with an ICCD (Andor Tech., iStar 334T) was used in this study. The 3600 lines/mm grating was used in this study which has a spectral resolution up to 0.019 nm. To further improve the light throughput of the spectrometer, an 800 μm × 75 cm UV enhanced fiber was used. Every measurement in experiment was repeated for ten times unless specially specified.

Seven certified pig iron samples (GSB 03-2582-2010 series) purchased from Pangang Group Research Institute Co. Ltd and eight low alloy steel samples purchased from NIST were used in this study. Concentrations of P and Cu which are the interference elements in pig iron samples and low alloy steel samples are listed in Tables 2 and 3, respectively.

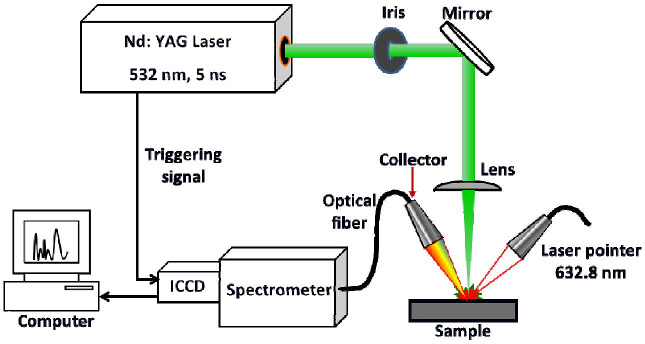

Fig. 1 Schematic diagram of the experiment setup.

Table 2 Concentrations (*wt. %*) of P and Cu in the pig irons (GSB 03-2582-2010 series).

	1#	2#	3#	4#	5#	6#	7#
P	0.011	0.033	0.045	0.087	0.072	0.168	0.306
Cu	(0.018)	(0.026)	(0.021)	(0.026)	(0.038)	(0.034)	(0.064)

Table 3 Concentrations (*wt. %*) of P and Cu in the low alloy steels from NIST

	1765	1766	1767	1265a	1761a	1762a	1763a	C1285
P	0.0052	0.002	0.0031	0.0011	0.042	0.0346	0.0123	0.072
Cu	0.0013	0.015	0.0014	0.0058	0.298	0.1186	0.042	0.37

3. Results and discussion

3.1 Qualitative analysis of P in pig iron

First of all, pig iron samples with 0.011%, 0.087%, 0.168% and 0.306% of P were used for qualitative study of P, in which the main P lines in the UV-VIS range were overviewed. A gate delay of 2 µs and a gate width of 5 µs were used in acquiring LIBS spectra.

Spectra of pig irons are shown in Fig. 2(a) and (b). P I 253.40 nm, 253.56 nm and 255.33 nm lines are overlapped by the iron matrix, which limits their use for chemical analysis. However, the interferences to P I 213.62 nm and 214.91 nm were just moderate, and the intensities of P I 213.62 nm and 214.91 nm are correlated with the P contents. Therefore, P I 213.62 nm and 214.91 nm are promising for detecting P in iron/steel. As P I 214.91 nm is interfered apparently weaker than that of P I 213.62 nm, P I 214.91 nm was selected as the main analytical line.

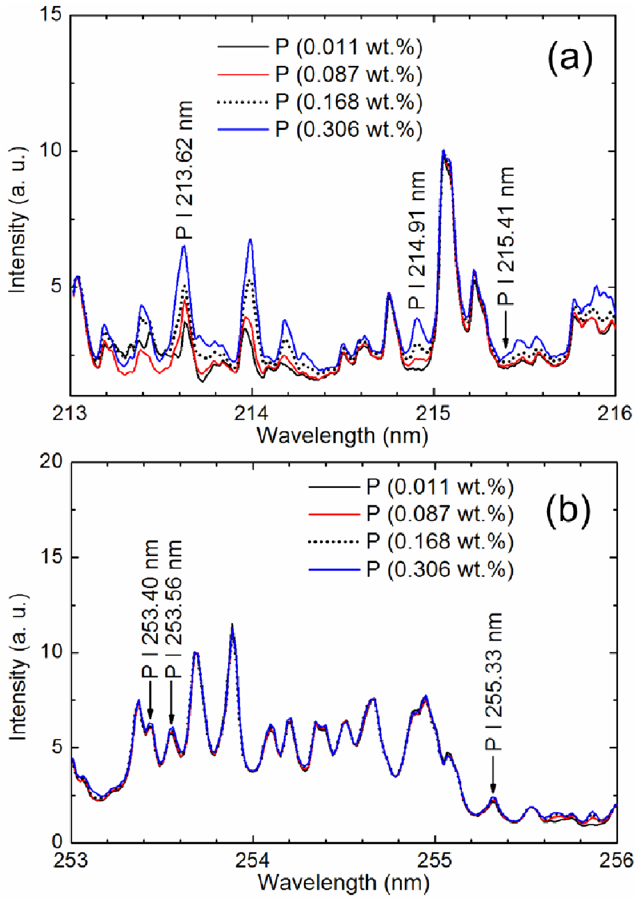

Fig. 2 Spectra of pig irons with 0.011%, 0.087%, 0.168% and 0.306% P contents. The main P lines in the UV-VIS spectral range are included in the spectra. The gate delay and gate width used in acquisition were 2 and 5 µs, respectively .

3.2 The interference from Fe and Cu to P I 214.91 nm

As shown in Fig. 2(a), even though the P content is as high as 0.306%, the corresponding intensity of P I 214.91 nm is still very weak compared to the iron lines on both sides (considerable interference to P I 214.91 nm). Therefore, the quality of the calibration curve of P I 214.91 nm is not so good. The R^2 factor and LoD are only 0.92 and 40 ppm, respectively. Therefore, the interference from the steel matrix to P I 214.91 nm cannot be neglected.

Generally, it is considered that iron matrix and Cu existing in steel will interfere the P detection.[24] For further understanding of the interference to the P I 213.62 and 214.91 nm lines, LIBS spectra of pure Fe, Cu, and P samples at different time periods were studied. The LIBS spectra at gate delays of 2 and 8 µs are shown in Fig. 3 (a) and (b), respectively.

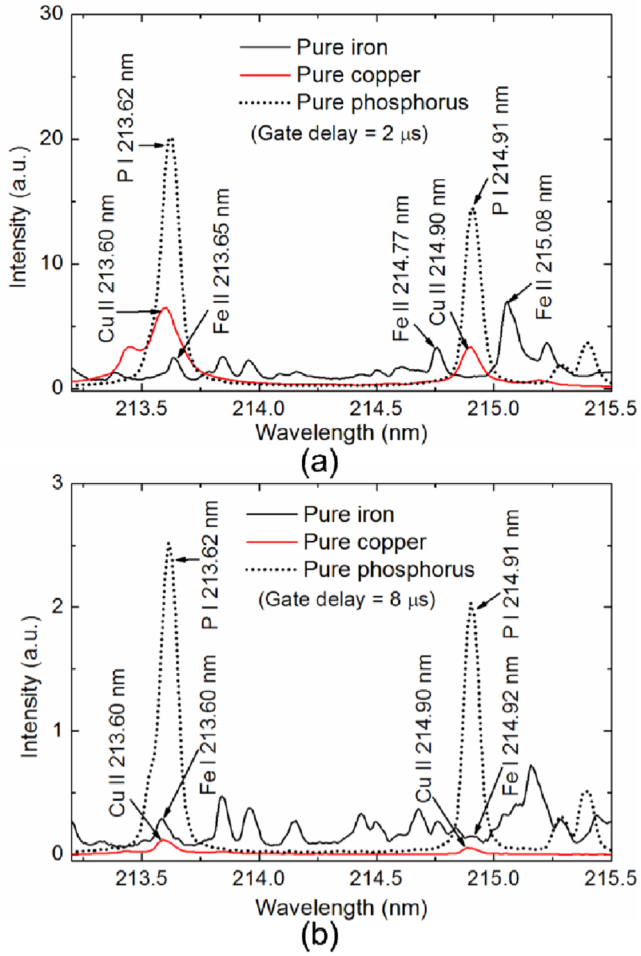

Fig. 3 LIBS spectra of pure Fe, Cu, and P in the range of 213 to 215.5 nm. The interference lines belonging to Fe and Cu of P I 213.62 nm, 214.91 nm have been marked.

As seen in Fig. 3(a), on the gate delay of 2 µs when the plasma was still hot, the main interference lines to P I 213.62 nm are Cu II 213.60 nm and Fe II 213.65 nm; the main interference lines to P I 214.91 nm are Cu II 214.90 nm and the tail parts of Fe II 214.77 nm and Fe II 215.08 nm. On a gate delay of 8 µs (Fig. 3 (b)) when the plasma was cooled down, the main interference lines to P I 213.62 nm are Cu II 213.60 nm and Fe I 213.60 nm; the main interfering lines to P I 214.91 nm are Cu II 214.90 nm and Fe I 214.92 nm.

It is known that ionic lines in laser-induced plasmas generally decay faster and have shorter lifetimes compared with those of atomic lines. Therefore, a longer gate delay maybe could help to reduce the interference from the ionic lines of Fe and Cu.

To evaluate the interference to P I 214.91 nm accurately, background equivalent concentration (BEC) of P I 214.91 nm was used, which is the ratio of intercept and slope of the calibration curve of P I 214.91 nm. The values of BEC as a function of the gate delay are shown in Fig. 4. The corresponding spectra of the pig irons are shown in Fig. 5. A gate width of 1 µs was used in the spectra acquisition. As can be seen in Fig. 4, the BEC of P I 214.91 nm at a gate delay of 1 µs was about 0.35 wt.%, which is high and affects the calibration. The lowest BEC was acquired at a gate delay of 8 µs when the interference from the ionic lines is negligible. After the gate delay of 8 µs, the BEC started to increase. This phenomenon could be explained as that the main interference to P I 214.91 nm after 8 µs is from the atomic lines of Fe such as Fe I 214.92 nm which last for much longer than P I 214.91 nm. As a result, BEC increases after 8 µs. Therefore, carefully choosing a proper gate delay and gate width is important to P detection in steel using LIBS.

The optimal gate delay and gate width can be deduced from Fig. 4. The lowest BEC corresponding to the lowest interference is obtained at a gate delay of 8 µs. However, the intensity of P I 214.91 nm at a gate delay of 8 µs is too weak. Therefore, a compromise between low BEC and high signal-to-noise ratio (SNR) needs to be made.

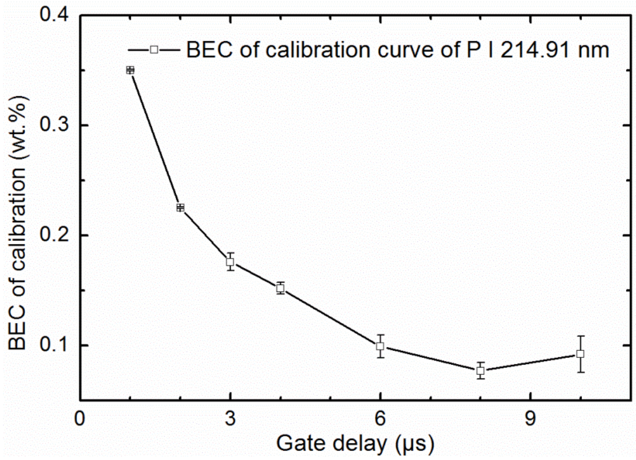

Fig. 4 Background equivalent concentration (BEC) of calibration curve of P I 214.91 nm (in pig iron) as a function of the gate delay. The gate width used in the acquisition is 1 µs.

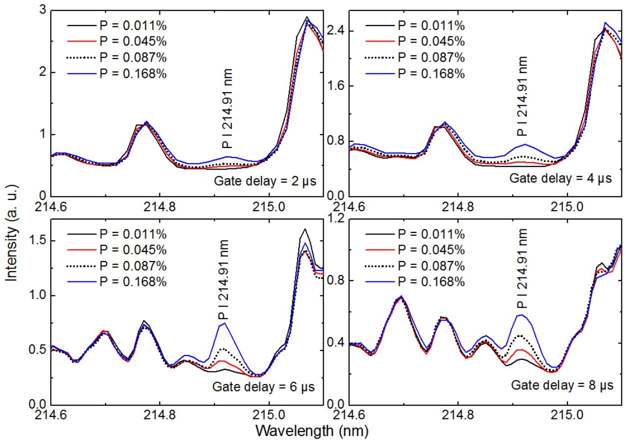

Fig. 5 LIBS spectra around 215 nm from the pig iron plasmas on the delay times of 2, 4, 6 and 8 µs, respectively. Position of P I 214.91 nm has been marked.

As we can see in Fig. 4, spectra acquired in the timescale of 6 to 11 µs (considering the gate width for Fig. 4 was 1 µs) were corresponding to a BEC as low as 0.1%. Therefore, in order to fully cover this time scale, gate delay of 6 µs and gate width of 5 µs were chose for quantitative analysis. As the difference between the matrices of pig iron and low alloy steel are limited and in order to keep the results comparable, the low alloy steels were analysed in the same condition with that of pig irons.

3.3 Influence of spectral resolution on the detection of P I 214.91 nm in steel

BEC of P I 214.91 nm in pig iron can be reduced to an acceptable level using a gate delay longer than 6 µs. However, as the spectrum of iron matrix around P I 214.91 nm is too complicated, a high spectral resolution is also required for detection of P I 214.91 nm in iron/steel samples.

LIBS Spectra of the pig iron samples with 0.168% P acquired with spectral resolutions of 0.019, 0.030, 0.039, and 0.071 nm have been shown in Fig. 6. The corresponding BEC values presented in Fig. 6 are 0.1%, 0.15%, 0.21% and 0.32%, respectively. Therefore, BEC of P I 214.91 nm is sensitive to the spectral resolution of the spectrometer. As seen in Fig. 6, the Fe I 214.84 nm line on the left side of P I 214.91 nm could be resolved from P I 214.91 nm well only when the spectral resolution is better than 0.03 nm. Therefore, to assure a low BEC value in calibration, a spectral resolution better than 0.03 nm is required.

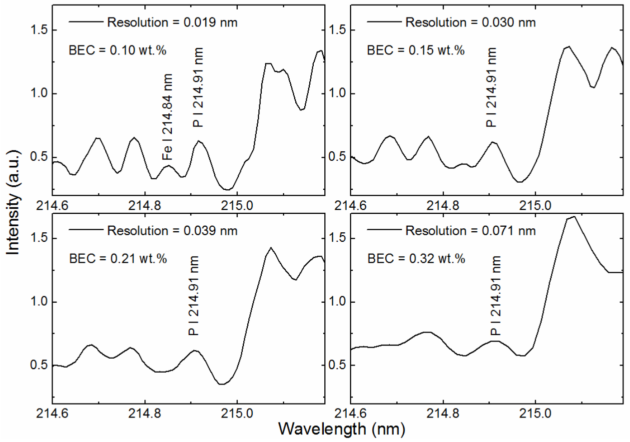

Fig. 6 Spectrum of pig iron (P = 0.168%) acquired with different spectral resolution.

3.4 The weak intensity of P I 214.91 nm in steel plasmas

The intensity of P I 214.91 nm in steel plasmas is weak and hence imposes another obstacle for P detection. To provide a measurement of the degree of weakness, Fe I 373.49 nm which is a strong Fe line and easy to be detected by most LIBS spectrometers, was used as a reference. Intensities of P I 214.91 nm and Fe I 373.49 nm were compared on gate delays of 1 µs and 6 µs. The results are presented in Fig. 7. In acquisition, the gain function of ICCD was not used and the slit width of spectrometer was also reduced to avoid the saturation of Fe I 373.49 nm.

On a gate delay of 1 µs, the intensity of P I 214.91 nm is just about 0.56% of that of Fe I 373.49 nm. At a gate delay of 6 µs, the intensity of P I 214.91 nm is just about 0.39% of that of Fe I 373.49 nm. Therefore, to detect P I 214.91 nm with sufficient SNR, a spectrometer with high light throughput is required or a large number of laser shots should be accumulated. Due to its high spectral resolution and high light throughput, a Czerny-Turner spectrometer with a spectral resolution of 0.03 nm and an ICCD camera are recommended for this application. In this study, with a moderate gain and sixty shots of accumulation, the SNR of P I 214.91 nm (0.168%) at a gate delay of 6 µs was better than 900.

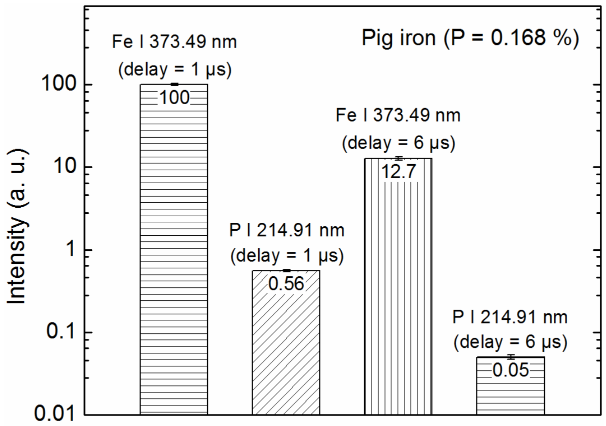

Fig. 7 Intensities of P I 214.91 nm and Fe I 373.49 nm on gate delays of 1 µs and 6 µs. To avoid the saturation of Fe I 373.49 nm at delay of 1 µs, the slit width of spectrometer was reduced and the gain function of ICCD was not used in acquisition.

3.5 Quantitative analysis of P in pig-iron and low-alloy-steel samples

Quantitative analyses of P contents were carried out for pig-iron and low-alloy steel samples, respectively. The gate delay and gate width used in acquisition were 6 and 5 µs, respectively. Sixty shots were accumulated for a high SNR of signal and a small fluctuation. Each acquisition was repeated for ten times.

Several well isolated iron lines with enough intensity had been tried to be used as the reference line of calibration. Fe I 218.40 nm and Fe I 214.44 nm were found to be the best for pig iron and low alloy steel, respectively. LoD was calculated by criteria of 3σ of the background noise which was measured by the standard deviation of the area in 209.56 - 209.68 nm.

The calibration curve for P in pig iron is shown in Fig. 8. The RSD of intensities of P I 214.91 nm is in the range of 1.5% - 4.9%, with the average is 3.1% which means the repeatability of the measurement is very good. The BEC of P I 214.91 nm is only 0.11% which is consistent with the result shown in Fig. 4. The R^2 factor of the calibration curve is 0.9992 and the LoD is 12 ppm. Both are comparable to the reported values (in Table 1) obtained in the VUV spectral range.

The calibration curve for P in low alloy steel is shown in Fig. 9. The RSD of intensities of P I 214.91 nm is in the range of 2% - 3.4%, with the average is 2.6%. The R^2 factor is 0.995 and the LoD is 9 ppm. It is interesting to notice that the BEC for the low alloy steels is only 0.05 wt.%, better than that of pig iron.

As an interference element in P detection, Cu concentrations in different samples are listed in Tables 2 and 3. However, as can be seen in Figs. 8 and 9, the existence of Cu has not considerably interfered the intensity of P I 214.91 nm. In other words, the interference from Cu II 214.90 nm to P I 214.91 nm is negligible after a gate delay of 6 µs. Therefore, the assumption that a longer gate delay helps to reduce the interference from ionic lines of Fe and Cu has been confirmed once more.

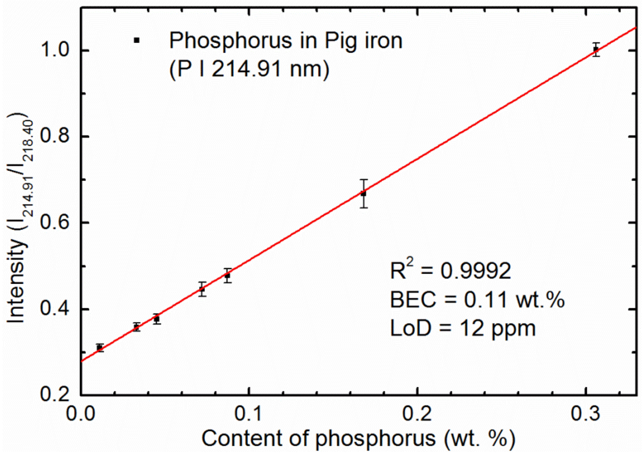

Fig. 8 Calibration curve for detecting P in pig iron using P I 214.91 nm.

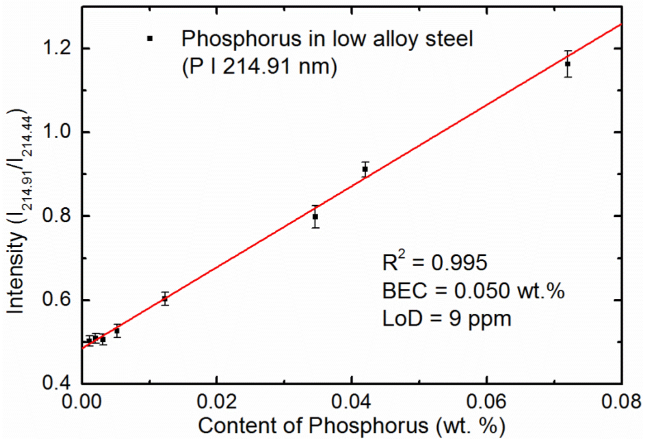

Fig. 9 Calibration curve for detecting phosphorus in low alloy steel. P I 214.91 nm was used.

4. Conclusions

Quantitative analysis of P in pig iron and low alloy steel in open air using a simple LIBS setup was carried out. The main P lines in pig iron samples were investigated. P I 214.91 nm was selected for further study because of the lowest interference from iron matrix. The Fe and Cu interferences to P I 214.91 nm were studied using both pure materials and pig iron samples, which shows that the main part of the interference to P I 214.91 nm is from Fe and Cu ionic lines. Interference can be reduced by choosing a proper gate delay. Spectral resolution and sensitivity were also found to be important for P detection in the UV-VIS spectral range. A Czerny-Turner spectrometer equipped with an ICCD camera with a resolution of 0.03 nm is recommended for this application. Quantitative analyses were successfully carried out both on pig-iron and low-alloy steel samples. The R^2 factors of the calibration curves are 0.9992 and 0.995, the BECs are 0.11 wt.% and 0.05 wt.%, and the LoDs are 12 ppm and 9 ppm, respectively. The interference from Cu in the pig iron and steel samples was not observed for P detection. Therefore, it is possible to detect P in iron/low alloy steel in open air using a simple LIBS setup.

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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