

DETERMINATION OF PHOSPHORUS IN STEEL USING INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

DOLOČEVANJE FOSFORJA V JEKLU Z ATOMSKO EMISIJSKO SPEKTROMETRIJO Z INDUKTIVNO SKLOPLJENO PLAZMO

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The standard test method for determining phosphorous^{1,2} is very time consuming and expensive. Arsenic, hafnium, niobium, tantalum, titanium, and tungsten interfere, especially when there are small quantities of phosphorous to be determined, and samples containing more than 0.1 % Cr must be treated separately.

Inductively coupled plasma atomic emission spectrometry offers a simple and quick method for the determination of phosphorus in steel. Here, the optimum operating conditions are described. The phosphorus line P(I) 214.914 nm, which has analytically usable detection limits, was taken into consideration. The multivariate method was used for the interpretation of the emission spectra from the inductively coupled plasma. The spectral interferences were identified and corrected.

For the method of phosphorus determination in steel the limit of detection (LOD) and the limit of quantification (LOQ) were estimated to be 0.1 $\mu\text{g g}^{-1}$ and 0.3 $\mu\text{g g}^{-1}$, respectively. The accuracy and traceability of the proposed method were tested by an analysis of closely matched matrix-certified reference materials.

Key words: steel, phosphorus determination, AES-ICP method

Standardna metoda za določevanje fosforja v jeklu^{1,2} je zelo zamudna in draga. Motnje arzena, hafnija, nioba, tantala, titana in volframa so posebno močno izražene pri določevanju nizkih vsebnosti fosforja. Vzorce, ki vsebujejo več kot 0,1 % Cr je treba obravnavati ločeno.

Atomska emisijska spektrometrija z induktivno sklopljeno plazmo (AES-ICP) pa nam omogoča hitro in enostavno določevanje fosforja v jeklu. Optimizirali smo operacijske pogoje. Obravnavali smo fosforjevo linijo P(I) 214.914 nm, ki ima analitsko uporabno mejo zaznavnosti. Emisijske spektre induktivno sklopljene plazme smo interpretirali z multi variacijsko metodo (Multicomponent Spectral Fitting Method), identificirali in eliminirali smo tudi spektralne interference.

Za metodo določevanja fosforja v jeklu smo določili mejo detekcije (LOD) in mejo določevanja (LOQ), ki sta 0,1 $\mu\text{g ml}^{-1}$ in 0,3 $\mu\text{g ml}^{-1}$. Pravilnost in sledljivost metode smo preverili z ustreznimi certificiranimi referenčnimi materiali.

Ključne besede: jeklo, določitev fosforja, metoda AES-ICP

1 INTRODUCTION

Commonly used standard methods for determining trace levels of phosphorus in iron, steel and alloys are based on the formation of phospho-vanado-molybdate, followed by its reduction to the molybdenum blue complex and its spectrophotometric determination^{1,2}. As, Hf, Nb, Ta, Ti, W and especially Cr interfere when detecting phosphorus, but these interferences can be partially overcome by the formation of complexes. Chromium can be removed by volatilization as chromyl chloride. Large amounts of iron (III) interfere, but may be masked with fluoride, the excess of which is complexed with boric acid. The reductants and certain coloured ions such as Cr(VI), Ni, Co, and Cu also interfere. The molybdo-vanado-phosphoric acid can be separated from many coloured ions by extraction with oxygen-containing solvents³. Many different indirect spectrophotometric methods were also suggested^{4,5}. The indirect determination of phosphorus by its complexation with molybdate, followed by the determination of molybdenum by atomic absorption spectrometry⁶⁻⁸ and

by inductively coupled plasma atomic emission spectrometry (ICP-AES)⁹ has also been reported.

ICP-AES has been used extensively for the determination of metallic constituents in environmental, industrial and even medical samples during recent years, but only a small amount of literature is related to the determination of non-metals. This is partly due to the location of prominent lines outside the conventional spectrometers, due to insufficient detection limits of these elements¹⁰, and spectral interferences remain a serious limitation of the technique¹¹, especially when the matrices are transition elements having line-rich spectra. Severe problems arise when the analyte exhibits only a few prominent lines. Phosphorus has only two prominent lines, at 213.618 and 214.924 nm, and all of them suffer serious interferences from iron and copper lines¹². For the next two P lines the detection limits are a factor of 4 and 5 higher, and they also suffer from Cu interferences. The Cu(II) 213.598-nm line is the fifth strongest line of copper according to Winge et al¹³. The P(I) 213.618-nm line lies on the edge of the Cu(II) 213.598-nm line,

which is very intense. The intensity ratio of P(I) 213.618/Cu(II) 213.598 increases with lowering the observation height¹⁴. Different optimal heights above the load coil were reported for phosphorus determination^{10,18}. It is hard to determine P at low levels in matrices containing Cu. The flow-injection-analysis (FIA) system incorporating a micro-column of activated alumina has been suggested for performing rapid analyte enrichment/ matrix removal for use in the ICP analysis of complex materials such as metallurgical samples¹⁵.

Multivariate methods for handling overlapped spectra in ICP–AES have been proposed^{16–22}. Metal alloys provide a particular analytical challenge because the major components of the material are spectrally rich and provide many potential spectral overlaps. The detection limit of an analyte is significantly improved when a mathematical treatment is applied to the emission spectra at multiple wavelengths near the peak maximum compared to peak height measurements that make use of only one band pass of information. The advantages of these multivariate methods are greatest in situations when the peaks of interference elements are present in the immediate vicinity of the analyte wavelength.

2 EXPERIMENTAL

2.1 Apparatus

All the data were collected on a Perkin-Elmer Optima 3100 RL ICP optical emission spectrometer, which is an Echelle spectrometer equipped with the SCD detection system. The measurements were made at the phosphorus line P(I) 214.914 nm, which is the most sensitive line.

The height above the load coil as critical components were determined (**Figure 1**). Other operating conditions are summarized in **Table 1**.

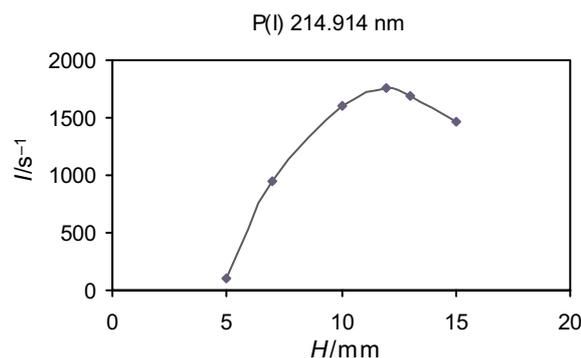


Figure 1: Observation heights H above the load coil
Slika 1: Višina opazovanja H nad tuljavo

Multi-component Spectral Fitting (MSF) was used to distinguish the analyte spectra from the interfering spectra. MSF was developed by PERKIN ELMER™ to achieve greater accuracy, using a full segment of the spectrum around the analyte wavelength²³. Mathematically, MSF uses a multiple, linear least-squares model²¹ based on an analysis of the pure solution being determined, the pure solution for each of the potentially interfering elements in the matrix, and the blank. There are no limits on the number of interfering elements that can be included in a model. Since only the peak shapes need to remain constant, the models are typically independent of concentration, plasma condition, and matrix effects.

2.2 Reagents

2.2.1 Hydrochloric acid ($\rho = 1.19$ g/ml), p. a. (Merck), diluted 1+1 with double-distilled water

2.2.2 Nitric acid ($\rho = 1.40$ g/ml), p. a. (Merck)

2.2.3 Phosphorus, standard solution, corresponding to 1000 mg/l, CertiPUR® Reference material (Merck).

Table 1: Operating parameters for the inductively coupled plasma spectrometer

Tabela 1: Operacijski pogoji delovanja atomskega emisijskega spektrometra z induktivno sklopljeno plazmo

SPECTROMETER	PERKIN ELMER, simultaneous, radial, model OPTIMA 3100 RL
Frequency	40 MHz, free-running
Power output	1200 W
Output power stability	< 0,1 %
ICP SOURCE	
Plasma torch	quartz / Al ₂ O ₃ injector – 2 mm
Coolant gas	15 L min ⁻¹
Auxiliary argon flow	0.5 L min ⁻¹
Nebulizer argon flow	0.7 L min ⁻¹
Height above load coil	12 mm
SAMPLE COMPARTMENT	
Spray chamber	Scott-type, Ryton
Nebulizer	Gem Type Cross-flow, pneumatic
Solution uptake rate	1 ml min ⁻¹
ANALYTICAL PARAMETER	
Flush time	30 s
Signal integration time	spectral profiling ON, auto read time = 20–40 s
Replicates	3

Phosphorus standard solutions, corresponding $100 \mu\text{g ml}^{-1}$ and $5 \mu\text{g ml}^{-1}$ should be prepared immediately before use by diluting with double-distilled water.

2.3 Procedure

2.3.1 MSF model

The solutions used to create the MSF model were single-element solutions of 5 mg ml^{-1} Fe, 1 mg ml^{-1} Cr, $500 \mu\text{g ml}^{-1}$ Ni, $100 \mu\text{g ml}^{-1}$ Mo, $25 \mu\text{g ml}^{-1}$ Cu, and $5 \mu\text{g ml}^{-1}$ P. They were prepared by the dissolution of commercial grade pure metals in acids (2.2.1, 2.2.2).

2.3.2 Calibration

A single-point calibration was performed with an aqueous solution of $5.0 \mu\text{g ml}^{-1}$ P (2.2.3.), which did not contain a steel matrix.

2.3.3 Recovery study

A matrix that resembles stainless steel (20 % Cr, 10 % Ni, 2 % Mo, 0.5 % Cu, and 75 % Fe) was prepared and spiked with different amounts of phosphorus standard solution ($100 \mu\text{g ml}^{-1}$, prepared by diluting the phosphorus ICP Standard (2.2.3)).

2.3.4 Trueness

1g of the standard reference steel samples (IRSID 282-1, BAM 2CrNiMoS, 451/1, BCS 404) was dissolved in 15 ml of concentrated HCl and 5 ml of concentrated HNO_3 . The insoluble carbon was filtered off and the filtrate was diluted to a final volume of 100 ml.

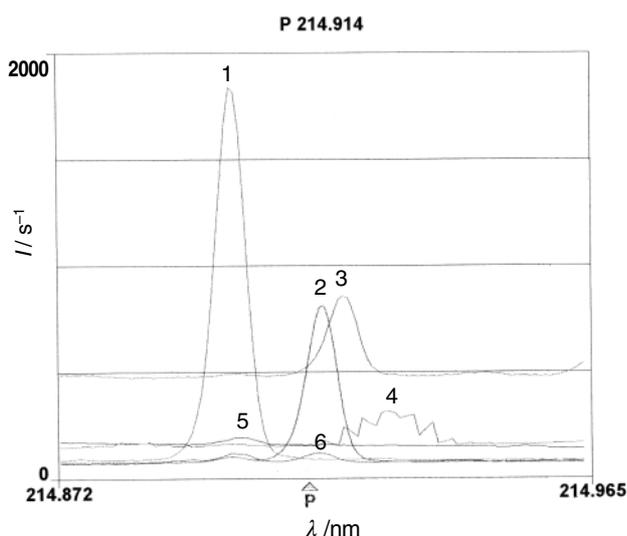


Figure 2: Pure-component spectral profiles recorded in the vicinity of the P-emission line at 214.914 nm; 5 mg ml^{-1} Fe (3), 1 mg ml^{-1} Cr (4), $500 \mu\text{g ml}^{-1}$ Ni (5), $100 \mu\text{g ml}^{-1}$ Mo (6), $25 \mu\text{g ml}^{-1}$ Cu (1) and $5 \mu\text{g ml}^{-1}$ P (2)

Slika 2: Spektralni profili čistih komponent v bližini P 214.914 nm emisijske linije; 5 mg ml^{-1} Fe (3), 1 mg ml^{-1} Cr (4), $500 \mu\text{g ml}^{-1}$ Ni (5), $100 \mu\text{g ml}^{-1}$ Mo (6), $25 \mu\text{g ml}^{-1}$ Cu (1) in $5 \mu\text{g ml}^{-1}$ P (2)

3 RESULTS AND DISCUSSION

The case studied is the determination of phosphorus in a matrix of steel at 214.914 nm.

A preliminary test showed that the P(I) 214.914-nm line was the strongest and the most suitable for the determination of phosphorus in a steel matrix. The phosphorus peak is completely obscured by the complex matrix spectrum. Wavelength scans around the phosphorus line are shown in **Figure 2** for the solutions of 5 mg ml^{-1} Fe, 1 mg ml^{-1} Cr, $100 \mu\text{g ml}^{-1}$ Mo, $25 \mu\text{g ml}^{-1}$ Cu, $500 \mu\text{g ml}^{-1}$ Ni, and $5 \mu\text{g ml}^{-1}$ P. The P(I) 214.914-nm line lies on the right-hand edge of the Cu(II) 214.901-nm line, on the left-hand edge of the Fe 214.921-nm line and on the left-hand side of the broadened Cr 214.034-nm line. The P peak complicates the spectrum so that two-point background correction methods would be insufficient. The analyte peak is in the "valley" between the Cr and Fe on the right-hand side, and Cu on the other side. The small changes in the concentrations of the interference ions will pose a problem because the background level will rise sharply in either direction away from the phosphorus peak.

Figure 3 shows the remaining phosphorus spectrum for a real sample after the correction of the continuum background and the Fe/Cr/Ni/Mo/Cu interferences by using the MSF file, which was previously built. The presence of the weak phosphorus signal is difficult to verify from a visual examination of the original spectrum, yet the MSF data reduction allows a selective determination of phosphorus from these data. An aqueous solution of $5.0 \mu\text{g ml}^{-1}$, which did not contain the matrix, was used for the calibration of the instrument. The phosphorus detection limit was measured in diluted acid (no matrix). The calculations of the LOD (as three times the random variation in the blank) and LOQ (as six times the random variation in the blank) were based on 10 consecutive replicate determinations. The efficiency of the constructed MSF model was obtained

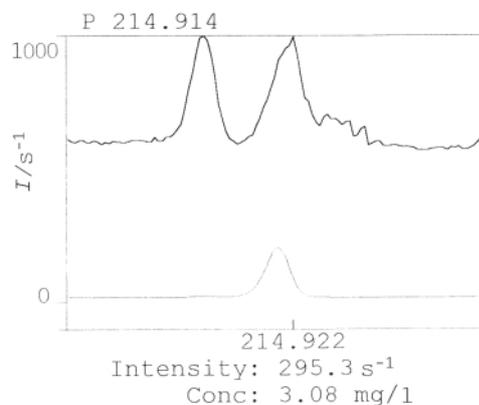


Figure 3: The measured spectrum consists of several components of stainless-steel matrix including P (bold line) and the corrected spectrum for P (thin line), applying the MSF technique

Slika 3: Merjeni spekter, ki vsebuje komponente matriksa, vključno P (odebeljena linija) in P spekter (tanka linija), korigiran z MSF-tehniko

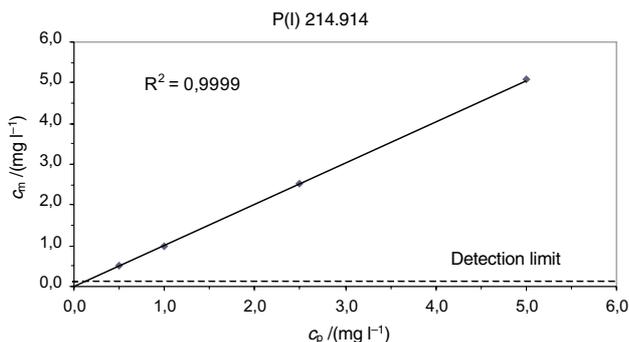


Figure 4: Determination of phosphorus in four solutions each containing the same steel (Fe/Cr/Ni/Mo/Cu) matrix (c_p – prepared concentration; c_m – measured concentration)

Slika 4: Določevanje fosforja v štirih raztopinah, ki vsebujejo enako jeklovo (Fe/Cr/Ni/Mo/Cu) osnovo (c_p – pripravljena koncentracija; c_m – merjena koncentracija)

Table 2: Accuracy assessment by means of certified reference materials

Tabela 2: Ocena pravilnosti z uporabo certificiranih referenčnih materialov

Sample	P/($\mu\text{g g}^{-1}$)		
	certified value	C (95 %)	determined value \pm std.dev
BCS 451/1	90	16	93 \pm 21
Carbon Steel			
BCS 404	500	13	490 \pm 16
Loa Alloy Steel			
IRSID 282-1	190	8	200 \pm 10
Highly Alloy Steel			
BAM 2CrNiMoS	346	14	340 \pm 19
Highly Alloy Steel			

by means of a recovery study. The concentrations of phosphorus were determined in four test solutions, each containing the same Fe/Cr/Ni/Mo/Cu matrix, prepared by the mixing of single-element solutions. The four solutions were "spiked" and contained 0.5, 1.0, 2.5 and 5.0 $\mu\text{g ml}^{-1}$ phosphorus, respectively. Three replicate determinations were made for each solution. The blank value of the matrix without a spike was subtracted (**Figure 4**). The accuracy of the method was determined by means of certified reference materials. Their compositions were very similar to the samples that are commonly analysed with the analytical method. Five test portions of each CRM were analysed according to the analytical procedure. The uncertainty component was evaluated experimentally from the dispersion of repeated measurements as a standard deviation. The analyses of certified reference materials also provide the traceability and validity of procedure (**Table 2**).

4 CONCLUSIONS

The use of the MSF algorithm for the determination of phosphorus in steel is demonstrated.

The spectral interferences that are caused by matrix elements could be overcome by using the full spectra information around the analyte peak. The pure phosphorus peak is extracted from the complex matrix spectrum. The intensity of the signal is quite low, but the stability of the measured signals, expressed as an RSD of the replicate measurement are satisfied when the recommended spectral profiling is chosen. The results for the spiked samples (**Figure 4**) show that the interferences of the matrix are successfully eliminated. The validity of the method is also proved by analysing certified reference materials. The results of the CRMs are in a good agreement with the certified values. The means of the determined values are inside the half-width confidence intervals, calculated as $C (95 \%) = \frac{t \cdot s_M}{\sqrt{n}}$,

where t is the appropriate Student's value and n is the number of acceptable mean values (s_M for n determinations were referred to in the certificate). The method is capable of determining 0.003 % of phosphorus in low steel. The advantage of the method is especially clear for highly alloyed steel, where the standard test method is not useful because of the high concentration of chromium as an interferent. The quantification of the measurement uncertainty will be discussed in a separate article that considers the overall precision, overall bias and the quantification of any uncertainties associated with effects incompletely accounted for in the overall performance studies.

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