

APPLICATION OF ICP-OES SPECTROMETRY FOR DETERMINATION OF HIGH CONCENTRATIONS OF SILICON IN CAST IRON AND STEEL

ZASTOSOWANIE TECHNIKI ICP-OES DO OZNACZEŃ WYSOKICH STĘŻEŃ KRZEMU W ŻELIWACH I STALI

The study investigates the possibility of applying induced plasma atomic emission spectrometry (ICP-OES) to determine silicon content exceeding 0.5% in iron-based samples. ICP-OES spectrometry requires liquid samples. Solid samples must be dissolved prior to the analysis. Dissolution of some types of steel requires strongly oxidising mixtures of inorganic acids. In such conditions, higher silicon contents tend to form insoluble oxides. Silicon oxides, in the form of amorphous sediment, precipitate on the bottom and walls of laboratory vessels. As a result, silicon determinations are strongly underestimated. The article presents the preparation of iron matrix based solutions for the determination of silicon-high concentrations using ICP-OES spectrometry.

Keywords: sample preparation, ICP-OES analysis, determination of Si content in steel

Celem pracy było zbadanie możliwości zastosowania techniki atomowej spektrometrii emisyjnej ze wzbudzeniem w plazmie indukowanej (ICP-OES), do oznaczania krzemu w zakresie stężeń przekraczających 0,5%, w próbkach na osnowie żelaza. Badanie składu chemicznego stali techniką ICP-OES wymaga przygotowania próbek w postaci roztworów. Roztworzenie niektórych gatunków stali wymaga zastosowania silnie utleniających mieszanin kwasów nieorganicznych. Warunki te, w przypadku wyższych zawartości krzemu, sprzyjają powstawaniu nierozpuszczalnego tlenku tego pierwiastka. Tlenek krzemu, w postaci amorficznego osadu, wytrąca się na dnie i ściankach naczyń laboratoryjnych. W efekcie, wyniki oznaczeń krzemu są silnie zaniżone. W artykule przedstawiono sposób przygotowania roztworów próbek na osnowie żelaza, do oznaczeń wysokich stężeń krzemu techniką ICP-OES.

Słowa kluczowe: przygotowanie próbki, analiza ICP-OES, oznaczanie Si w stali

1. INTRODUCTION

Silicon is one of the key components in iron alloys. Its presence improves strength and hardness of steels and enhances their corrosion resistance [1, 2]. Depending on a sample's physical form and the capability of analytical laboratory equipment, the determination of silicon content in iron-based materials can be carried out by number of instrumental techniques and classical methods. Analytical techniques that require dissolution of test material are usually used when steel samples in the form of chips, small pieces or powders need to be analysed. Traditional gravimetric methods involve separating the element from the sample as silicic acid and hydrated silica. Silicon compounds separated from the sample matrix are exposed to dehydration agents and calcining processes to obtain pure silicon dioxide. Isolated silica precipitate is the starting point for the gravimetric method [3–7]. Gravimetric methods for determination of silicon provide reliable and precise results. However, the time required and laboriousness

of analysis, as well as the possibility of determining only one component of the sample, are serious limitations.

ICP-OES spectrometry allows for the determination of a wide range of steel components from a single sample solution. Steel digestion requires the use of an appropriate acid or acid mixture, depending on the proportion of alloying elements present in the sample material [8]. After dissolution, the silicon present in the sample transfers into the solution in the form of silicic acids. Under suitable conditions, silicic acids undergo polymerisation that leads to the formation of compounds that are difficult to dissolve, usually in the form of amorphous precipitates [9, 10]. The precipitation phenomenon, which is essential for silicon gravimetric analytical methods, in case of the ICP-OES technique prevents the correct determination of the analyte.

The goal of this paper was to investigate the method for the dissolution of steel samples with elevated silicon content that would allow correct determination results using the ICP-OES spectrometry. The results were compared

with method used so far in laboratories for the digestion of iron-based samples with a low content of silicon [11]. This method provides for the determination of silicon in steel, cast iron and pig iron in the range of 0.005–0.5 weight %. The validity of the procedure was monitored by gravimetric method using perchloric acid as a dehydration agent.

2. EXPERIMENT

2.1. SAMPLE PREPARATION PROCEDURE

Two series of standard material solutions were prepared for ICP-OES measurements (Table 1). The first set (series I) was prepared by dissolving a 0.25 g sample in diluted nitric acid (V) ($\text{HNO}_3 + \text{H}_2\text{O}$, 1:1) or a mixture of nitric acid (V) and hydrochloric acid ($\text{HNO}_3 + \text{HCl}$, 1:3). The acid mixture was used for materials that contained alloying elements. After gentle heating, driving off the brown fumes of nitrogen oxides and complete digestion of the sample, the solutions were transferred to 100 cm³ glass volumetric flasks.

In the second set of solutions (series II), 0.25 g samples of standard materials were dissolved in a mixture of hydrochloric acid, nitric acid (V) and hydrofluoric acid ($\text{HCl} + \text{HNO}_3 + \text{HF}$, 10:2:3). Due to the presence of hydrofluoric acid, the digestion process was carried out in plastic beakers. The contents of the beakers were heated gently. This precaution was intended to reduce the possibility of analyte loss in the form of easily volatile silicon tetrafluoride. The obtained solutions were diluted to 100 cm³ in plastic flasks. In parallel, gravimetric determination of silicon based on dehydration of silica in perchloric acid (VII) (HClO_4) was performed for all reference materials.

2.2. MEASUREMENT CONDITIONS

Silicon determinations were performed using an Agilent 5100 SVDV ICP-OES spectrometer. During the measurement, the spectrometer was equipped with a sample delivery system resistant to hydrofluoric acid: “One Neb” nebuliser, a double-pass plastic spray chamber, and a plasma torch with alumina injection tube. The development of an analytical program for the ICP-OES spectrometer required the establishment of a number of the spectrometer’s operating parameters to ensure optimum conditions for the determination of silicon. A possibility of spectral interference was investigated. For this purpose, recorded silicon emission spectrum was superimposed over the spectrum of potential interfering elements, which are common components of the steel sample (Table 2).

The effect of plasma generator power and the effect of the argon flow rate through the nebuliser on the silicon line emission intensity were investigated. The study was conducted by recording the intensity of silicon lines and background emission intensity around the lines. Then, the ratio of silicon line intensity to background emission intensity was evaluated. The effect of plasma generator power

on silicon emission spectrum was studied in the range of 700–1500 W. The study of the dependence of silicon line intensity and background emission in its surroundings on the nebuliser argon flow rate was carried out in the range of 0.1–1.1 dm³/min. In both cases the spectrum was recorded in an axial view of plasma discharge, using a nebuliser and a mist chamber made of plastic. Optimization studies enabled the possibility to develop an analytical program for the Agilent 5100 ICP-OES spectrometer. The prepared analytical program (Table 3) allowed for selective determination of elemental content, while ensuring adequate signal quality.

Table 2. Identified elements interfering with silicon emission lines

Tabela 2. Zidentyfikowane pierwiastki interferujące linie emisyjne krzemu

Element	Wavelength [nm]	Interfering element
Si	251.621	Mo, W
	251.920	Ti, Fe, W
	252.411	W, Mo
	288.158	W

Table 3. ICP-OES instrumental conditions for silicon content >0.5 weight % in steel

Tabela 3. Program spektrometru ICP-OES do pomiarów zawartości krzemu >0,5% wag. w stali

Wavelength [nm]	Si 251.611
Plasma view	axial
Radio frequency power [W]	1200
Nebulizer gas flow [dm ³ /min]	0.8
Plasma flow [dm ³ /min]	12
Pump speed [rpm]	20
Nebulizer	One Neb
Nebulization chamber	plastic, double pass
Torch	corundum injector

2.3. SPECTROMETER CALIBRATION

The calibration of the spectrometer was carried out using synthetic solutions. A stock solution (single element) of silicon with a concentration of 1000 µg/cm³ was prepared. An appropriate volume of Si stock solution was introduced into 100 cm³ plastic volumetric flasks. A series of solutions were obtained in a concentration range from 0.48% to 5% silicon with respect to a 0.25 g sample weight (Table 4). The resulting calibration curve of Si 251.611 nm line is shown in Fig. 1. An additional solution of 0.25 g iron was introduced into each flask to simulate the presence of Fe matrix. The contents of the flasks were made with demineralised water.

Table 1. Reference materials used in tests

Tabela 1. Materiały odniesienia zastosowane w badaniach

Reference sample	BCS 335	BCS 342	MBH 11XC10D	BCS 317	Brammer Standards 181B
steel grade	austenitic steel	ferritic steel	cast iron	low carbon steel	high manganese, stainless steel
certified Si, [weight %]	0.67	0.92	1.89	3.49	3.94

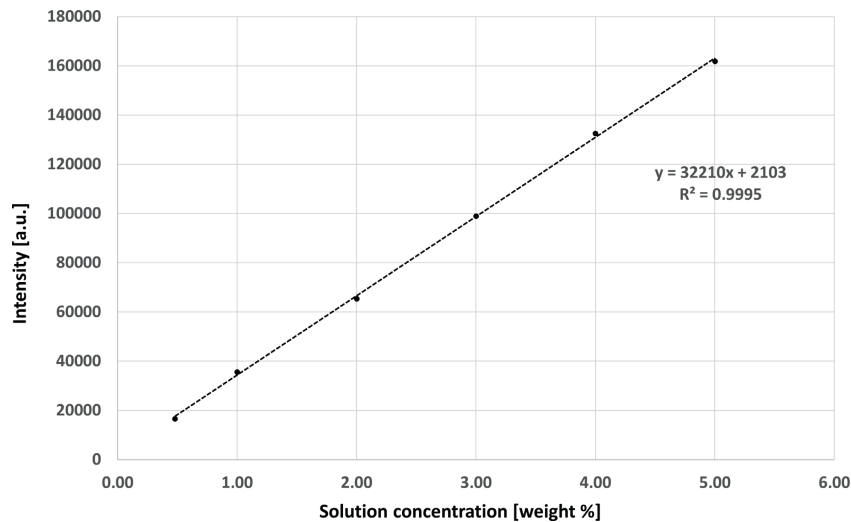


Fig. 1. Calibration curve for Si 251.611 nm line in range 0.48–5.0%

Rys. 1. Wykres kalibracyjny dla linii Si 251,611 nm w zakresie 0,48÷5,0%

Table 4. Concentrations of synthetic calibration silicon solutions

Tabela 4. Stężenia syntetycznych roztworów kalibracyjnych krzemu

Si stock solution concentration [$\mu\text{g}/\text{cm}^3$]	Introduced volume [cm^3]	Si concentration in obtained solution	
		[$\mu\text{g}/\text{cm}^3$]	[%]
1000	1.2	12	0.48
	2.5	25	1.0
	5.0	50	2.0
	7.5	75	3.0
	10.0	100	4.0
	12.5	125	5.0

3. RESULTS AND DISCUSSION

The results of silicon determination using the ICP-OES technique (series I and series II) compared with the results obtained using the reference gravimetric method are shown in Table 5.

For the first series (series I) of solutions, the results of silicon determination using the ICP-OES technique deviated from the certified values for each reference material. For lower silicon contents, analyte recovery oscillated in the range of 85–90%. For standards with higher silicon

content, analyte recovery value was about 60%. In the method of digestion applied for series I, the higher content of silicon in the sample led to formation of a greater amount of insoluble silicon compounds. In the second series (series II) of measurements, analyte recovery was not less than 96%, similarly to the gravimetric reference method. The obtained results of silicon determinations indicated a better efficiency of the sample digestion process in the mixture containing hydrofluoric acid. The complex properties of hydrofluoric acid allowed for higher silicon concentrations to be preserved in the solution. The high recovery values also indicate that there was no loss of silicon in the form volatile fluoride compound during sample digestion process.

The mixture of hydrochloric acid, nitric acid (V) and hydrofluoric acid prepared in 10:2:3 ratio, enabled effective preparation of sample solutions, regardless of steel grade and presence of alloying elements.

4. SUMMARY

The feasibility of an effective dissolution method for steel samples with high silicon content in terms of determination using the ICP-OES technique was investigated. The sample preparation procedure was effective irrespective of steel grade and presence of alloying elements. The results obtained with ICP-OES spectrometry were comparable to

Table 5. Results of silicon determinations obtained using the ICP-OES technique and gravimetric method

Tabela 5. Wyniki oznaczeń krzemu uzyskane techniką ICP-OES oraz metodą grawimetryczną

Reference material	BCS 335	BCS 342	MBH 11XC10D	BCS 317	Brammer Standards 181B
Certified Si value [weight %]	0.67	0.92	1.89	3.49	3.94
ICP-OES series I results [weight %]	0.57±0.04	0.83±0.04	1.12±0.06	2.13±0.06	2.11±0.06
ICP-OES series I: recovery [%]	85	90	59	62	53
ICP-OES series II results [weight %]	0.64±0.04	0.90±0.05	1.85±0.06	3.52±0.08	3.93±0.09
ICP-OES series II: recovery [%]	96	98	98	102	99
Gravimetric method results [weight %]	0.65±0.05	0.91±0.07	1.90±0.14	3.49±0.23	3.92±0.26
Gravimetric method recovery [%]	97	99	101	100	99

those obtained with reference gravimetric method, while the analysis was less time-consuming. In the performed study, the determination of silicon using the gravimetric method took 2–3 days for up to five samples. In comparison, time required to perform determination using ICP-OES spectrometry was one day for about 20 samples.

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