

Študij optimalnih pogojev za analizo kovinskih materialov z metodo ICP atomske emisijske spektrometrije

Investigation of Optimal Conditions for Metal Analysis by ICP Atomic Emission Spectrometry

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Študirali smo optimalne pogoje in aparativne parametre za analizo nikljevih zlitin s sekvenčno atomsko emisijsko spektrometrijo. Razvili smo metodo multielementne analize za določanje Ni, Co, Cr, Mo, Ti (60 do 2 %) ter Al, Fe, Mn, Cu in Si (1 do 0.005 %). Študirali smo spektralne interference za vse prisotne elemente. Izbrali smo optimalne valovne dolžine, ter določili občutljivost, mejo zaznavnosti, korekcijske faktorje in reproduktivnost rezultatov. Točnost rezultatov smo preverili s certificiranimi referenčnimi materiali nikljevih zlitin podobnih sestav.

The optimal conditions and determination parameters for analysis of nickel base alloys by sequential ICP atomic emission spectrometry were studied. A method for determination of major Ni, Co, Cr, Mo, Ti (~60 to 2 w/w %) and minor components Al, Fe, Mn, Cu Si (~1 to 0.05 w/w %) using a single sample preparation technique was developed. Actual spectral interferences due to the influence of any present element were identified by wavelength scans near analyte wavelengths for Ni, Co, Cr, Mo, Ti, Al, Fe, Mn, Cu and Si. Optimal spectral lines, detection limits, sensitivities, additive correction factors and reproductivity of results were established. The accuracy of the results was checked with different certified materials of similar composition.

UVOD

Za hitro analizo kovin in zlitin se običajno najbolj uporabljata metodi emisijske spektrometrije z vzbujanjem z iskro in rentgenska fluorescenčna analiza. Alternativno možnost za analizo metalurških vzorcev predstavlja atomska emisijska spektrometrija z induktivno sklopiljeno plazmo (ICP AES). Prednosti metode so predvsem možnost multielementne analize, dobra občutljivost, široko linearno koncentracijsko območje ter malo kemijskih motenj. V literaturi zasledimo številne publikacije o teoretičnih osnovah, operativnem razvoju, napredku in aplikacijah ICP AES za analizo kovinskih materialov^{1,2,3,4,5,6,7}. Vsak sistem zahteva specifičen način raziskovanja in kritično ovrednotenje rezultatov za izbiro optimalnih parametrov analize in dosego optimalne kombinacije občutljivosti, stabilnosti ter razmerja signal — ozadje za določen element.

To delo obsega raziskave za izdelavo analizne metode, ki omogoča določanje desetih elementov na različnih koncentracijskih nivojih v vzorcih nikljevih zlitin, tipa Nimonic.

EKSPERIMENTALNO DELO

Meritve smo izvršili s sekvenčnim vakuumskim emisijskim spektrometrom z ICP izvorom, firme Applied Research Laboratories (ARL), model 3520 OES. Karakteri-

INTRODUCTION

Routine analysis of metals and their alloys are commonly performed by spark emission spectrometry or x-ray fluorescence. Other alternative for analysis of metallurgical samples represents inductively coupled plasma atomic emission spectrometry with its multielement capability, good sensitivity, wide linear calibration ranges and freedom from chemical-type interferences. There are numerous publications on theory, progress and application of ICP atomic emission spectrometry for metal analysis^{1,2,3,4,5,6,7}. Each system requires specific way of investigation and critical evaluation of results to get optimal operating parameters giving the best combination of sensitivity, stability and line to background ratios for elements concerned.

The present paper reports about a single analytical method applicable to the determination of ten elements at major and minor constituent levels in samples of nickel base alloys of Nimonic type.

EXPERIMENTAL

Equipment

Applied Research Laboratories (ARL) 3520 OES vacuum sequential scanning inductively coupled plasma emission spectrometer was used for all measurements. The instrument specifications and operating conditions are given in Table 1.

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stike aparature in eksperimentalni parametri so navedeni v tabeli 1.

Tabela 1: Karakteristike aparature in eksperimentalni parametri

APARATURA:	ARL, model 3520 OES sekvenčni, vakuumski — spektrometer, ICP izvor
Spektrometer	
Monohromator:	1 m premera, Paschen-Runge nastavitev
Uklonska mreža:	1080 zarez/mm
Spektralno območje:	170—797 nm
Širina reže, primarna:	20 μ m
Širina reže, sekundarna:	50 μ m
RF generator	
Frekvenca:	27.12 MHz
Moč:	1200 W
Reflektirana moč:	< 5 W
ICP izvor	
Gorilec:	koncentričen, kremenčev, tip Fassel
Pretok Ar, hladilni:	12 l/min.
Pretok Ar, plazma:	0.8 l/min.
Pretok Ar, nosilni:	0.32 l/min.
Višina opazovanja:	15 mm nad tuljavo
Vnašanje raztopine	
Razpršilec:	steklen, tip Meinhard
Hitrost sesanja raztopine:	2 ml/min.
Analizni parametri	
Čas izpiranja:	15 s
Čas integracije:	2 s

Priprava vzorca

50 mg vzorca (v obliki finih ostružkov) zatehtamo v 100 ml čašo in previdno raztapljamo v 20 ml kislinke mešanice $H_2O : HCl : HNO_3 = 3 : 2 : 1$. Raztopino rahlo segrevamo, da se vzorec popolnoma raztopi, po potrebi filtriramo. Raztopino ohladimo na sobno temperaturo, prelijemo v 500 ml merilno bučo in dopolnimo do 500 ml z deionizirano vodo. Vzoredno pripravimo slep vzorec.

Umerjanje

Umeritvene krivulje smo izdelali s pomočjo multielementnih standardnih raztopin in s certificiranimi referenčnimi materiali nikljevih zlitin (BAS, MBH), ki smo jih raztapljali na enak način kot vzorce.

Multielementne standarde raztopine za umerjanje smo pripravili iz čistih kovin ali soli, ki smo jih raztopili v kislini mešanici oziroma v vodi.

REZULTATI IN DISKUSIJA

Prvi korak pri razvoju analizne metode je izbira in ovrednotenje primernih spektralnih črt, ki so optimalne za posamezni element glede na sestavo vzorca in njegovo koncentracijsko območje. Možnost izbire med več emisijskimi črtami za posamezni element dovoljuje določanje več elementov v istem vzorcu v različnih koncentracijskih nivojih pri enakem faktorju razredčenja.

Spektralne interference, ki so posledica vpliva kate-regakoli prisotnega elementa v vzorcu zaradi prekrivanja spektralnih črt, smo ugotavljali z opazovanjem profila spektralnih črt pri ustreznih valovnih dolžinah za elemen-

Table 1: Instrumentation and operating conditions

APPARATUS:	ARL, model 3520 OES Sequential, vacuum spectrometer, ICP source
Spektrometer	
Monochromator:	1 m radius, Paschen-Runge mounting
Grating:	1080 grooves/mm
Spectral range:	170—797 nm
Slit width, primary:	20 μ m
Slit width, secondary:	50 μ m
RF Generator	
Frequency:	27.12 MHz
Incident power:	1200 W
Reflected power:	< 5 W
Plasma	
Plasma torch:	Three concentric quartz tubes, Fassel type
Argon flow rate, coolant:	12 l/min.
Argon flow rate, plasma:	0.80 l/min.
Argon flow rate, carrier:	0.32 l/min.
Observation height:	15 mm above load coil
Sample introduction	
Nebuliser:	glass concentric type (Meinhard)
Solution uptake rate:	2 ml/min.
Analysis parameters	
Flow time:	15 s
Integration time:	2 s

Sample preparation

500 mg of sample in the form of fine drillings was weighed into a 100 ml beaker and carefully dissolved in 20 ml of 3 : 2 : 1 mixture of $H_2O : HCl : HNO_3$. The solution was heated gently to complete the dissolution, and filtered where necessary. After cooling to room temperature, the solution was made up to 500 ml with deionised water in the volumetric flask. An acid blank of the appropriate concentration was also prepared.

Calibration

Calibration curves were obtained from direct intensity measurements made on multielement standard solutions or solutions of certified reference materials, supplied by the BAS (BCS) and MBH (Willan Metals Limited — Rotherham).

Stock calibration multielement standard solutions were prepared from pure metals or salts, dissolved in high purity acid mixture or deionised water, respectively.

RESULTS AND DISCUSSION

The first step of investigation was the selection and evaluation of the wavelengths that are the most suitable for each element in a particular matrix. The flexibility of utilizing many emission lines for each element allows to analyse different elements in a sample at various concentration levels with a single dilution factor. Spectral interferences due to the influence of any present element in the sample were identified by wavelength scans near analyte wavelengths (± 0.2 nm) for Ni, Co, Cr, Mo, Ti, Al, Fe, Mn, Cu and Si. The wavelengths for particular element were selected from the available lists of ICP atomic emission lines by Boumans⁸ considering their sen-

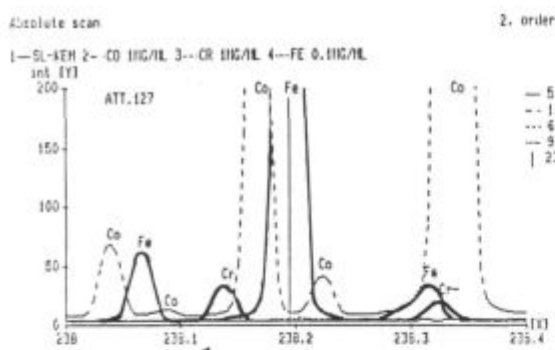
te Ni, Co, Cr, Mo, Ti, Al, Fe, Mn, Cu in Si v območju ± 0.2 nm od maksimuma izbrane spektralne črte. Valovne dolžine za posamezni element smo izbrali z liste možnih ICP AES spektralnih črt po Boumansu⁸, upoštevajoč njihovo občutljivost, čim manjše interference ter nizko in konstantno ozadje.

Rezultati teh poskusov so pokazali, da korekcija ozadja ni potrebna. Kot je prikazano na **sliki 1 in 2**, smo ugotovili le spektralno interferenco kobalta na 238.204 nm Fe črti in molibdena na 251.611 nm Si črti, kar povzroča napako pri določanju železa oziroma silicija. Majhen peak, ki ga opazimo na obeh Si spektralnih črtah v prisotnosti titana (**slika 2**), pripisujemo kontaminaciji Ti standarda s silicijem, ki je nastala pri pripravi standardne raztopine z raztapljanjem titana v kislini mešanici HF-HNO₃.

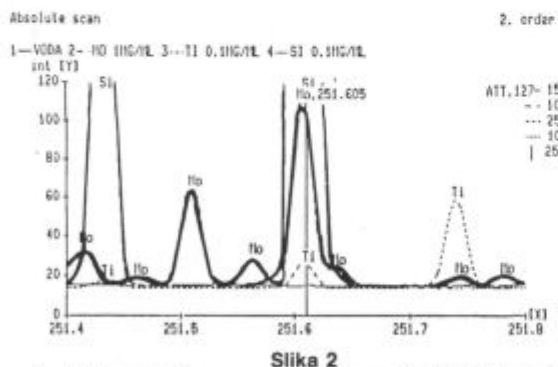
Izvršili smo korekcijo za železo in silicij glede na moteče elemente. Na **sliki 3** prikazujemo primerjalne rezultate določanja silicija v različnih standardnih vzorcih nikljevih zlitin s korekcijo motečega elementa (Mo) in brez nje.

Na osnovi rezultatov preliminarne poskusov smo za vsak element izbrali optimalne spektralne črte, čas izpiranja, čas integracije, pretok argona in druge parametre, ki so prikazani v **tabelah 2 in 1**. Izdelali smo umeritvene krivulje s pomočjo multielementnih standardnih raztopin in certificiranih referenčnih materialov, pri čemer smo v obeh primerih dobili skoraj identične signale.

V **tabeli 2** so zbrani podatki za valovne dolžine uporabljenih spektralnih črt, občutljivost, mejo zaznavnosti, relativni standardni odklik, koncentracijsko območje in korekcijske faktorje. Meja zaznavnosti je definirana kot



Slika 1
Spektralna interferenca kobalta na Fe 238.204 nm liniji
Fig. 1.
Spectral interference of cobalt on Fe 238.204 nm line



Slika 2
Spektralna interferenca molibdena na Si 251.611 nm liniji
Fig. 2
Spectral interference of molybdenum on Si 251.611 nm line

sensitivities, freedom of interferences and a constant, low background structure.

Graphic spectral scans had shown that no background correction was necessary. As indicated in **Fig. 1 and 2** only the presence of cobalt at 238.204 nm Fe line and presence of molybdenum at 251.611 nm Si line could introduce an error in iron and silicon determination, respectively. The small peak of Ti standard observed on the both Si lines (**Figure 2**) was due to the contamination of Ti standard with silicon at preparation of this standard solution by dissolution of titanium with HF-HNO₃ acid mixture.

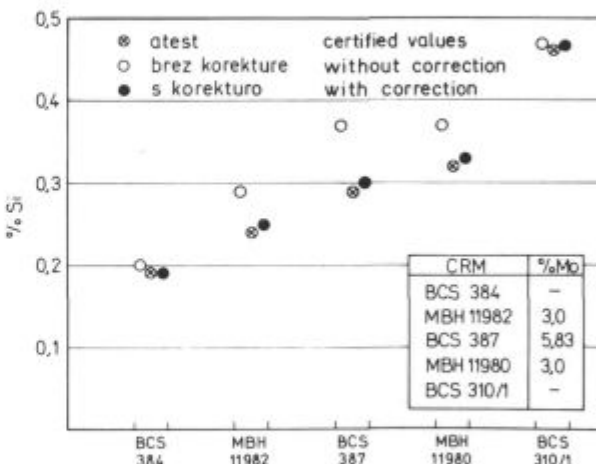
The correction for Fe and Si considering the mentioned interfering elements was made. Comparison results of Si determination in different certified reference materials with and without correction of interfering element (Mo) are presented in **Fig. 3**.

On basis of results obtained by preliminary study optimal spectral lines, flush time, integration time, argon carrier flow rate and other parameters were selected for each element (**Table 2, Table 1**).

Calibration curves and regression on the basis of multielement standard solutions and certified reference materials were made. Signals of mostly identical relative intensities were obtained for multielement standard solutions and solutions of certified reference materials.

Spectral lines used, sensitivities, detection limits, relative standard deviations, concentration ranges and correction factors for investigated elements are summarized in **Table 2**. Detection limit is defined as twice the standard deviation of the fluctuation of the blank signal divided by the slope of the linear calibration curve⁹. It was calculated from the data of 10 successive intensity measurements of the blank value.

The accuracy of the method was checked with different reference materials of similar composition. Composition results of ICP and certified values for two BCS standards are given in **Tabele 3**. The presented standard deviations were obtained with frequent successive measurement of the same sample. The results generally indicated good agreement within reported standard deviations for all elements, except for nickel and copper. The worst reproducibility and accuracy of results was



Slika 3
Primerjalni rezultati za silicij z in brez korekcije motečega elementa (Mo)
Fig. 3
Comparison results of Si determination with and without correction of interfering element (Mo)

Tabela 2: Optimalni pogoji in ugotovljeni parametri za analizo nikljevih zlitin**Table 2:** Optimal conditions and established data for ICP analysis of nickel alloys

Element Element	Valovna dolžina (nm) Wavelength (nm)	Faktor občutljivosti Attenuator- position	Občutljivost S_{ICP} (rel. enote-za 1ppm) Sensitivity S_{ICP} (rel. units-for 1ppm)	Meja zaznavnosti D_L (μg/ml) Detection Limit D_L (μg/ml)	RSD % RSD %	Območje % Range (w/w %)	Aditivna korekcija Additive correction	
							moteči element Interfering element	koefficient Coefficient
Ni	221,647	125	9,0	0,006	0,59	58—62		
Co	228,616	127	17,1	0,006	0,73	14—17		
Cr	205,552	127	4,8	0,007	0,78	9—13		
Mo	202,030	127	3,0	0,013	0,86	3—6		
Ti	307,864	120	101,5	0,014	0,80	2—5		
Al	309,278	120	38,1	0,037	0,60	0,2—6		
Fe	238,204	120	13,5	0,008	1,0	0,2—0,8	Co	—0,0008
Si	251,616	127	21,3	0,011	2,1	0,2—0,5	Mo Mn	—0,0139 —0,0065
Mn	294,920	127	325,8	0,002	1,1	0,1—0,4		
Cu	327,396	127	298,0	0,002	2,5	0,01-0,05		

Tabela 3: ICP in certificirane vrednosti — primerjalni rezultati v %**Table 3:** ICP and certified values comparison results (all results in w/w %)

Element	BCS 310/1		BCS 387	
	ICP	Atest	ICP	Atest
Ni	58,2 ± 0,52	58,6 (58,5—58,7)	41,4 ± 0,38	41,9 (41,8—42,0)
Co	16,80 ± 0,11	17,0 (16,88—17,2)	0,23 ± 0,002	0,21 (0,21—0,23)
Cr	19,44 ± 0,14	19,45 (19,37—19,52)	12,44 ± 0,02	12,46 (12,40—12,52)
Mo	0,035 ± 0,002	n.d.	5,80 ± 0,05	5,83 (5,75—5,85)
Ti	2,41 ± 0,01	2,43 (2,39—2,47)	2,92 ± 0,016	2,95 (2,88—3,04)
Al	1,055 ± 0,003	1,06 (1,02—1,09)	0,27 ± 0,002	0,24 (0,22—0,25)
Fe	0,27 ± 0,003	0,25 (0,24—0,27)	35,72 ± 0,25	36,0 (35,8—36,1)
Mn	0,35 ± 0,004	0,35 (0,34—0,37)	0,085 ± 0,0004	0,08 (0,080—0,085)
Cu	0,04 ± 0,001	n.d.	0,045 ± 0,0003	0,032 (0,029—0,033)
Si	0,47 ± 0,01	0,46 (0,44—0,47)	0,30 ± 0,005	0,28 (0,26—0,30)

dvakratni standardni odklik slepe vrednosti, deljen z naklonom umeritvene krivulje⁸. Meja zaznavnosti je izračunana na osnovi podatkov desetkratne zaporedno izmerjene intenzitete slepe vrednosti.

Točnost metode smo preverili na različnih standardih nikljevih zlitin podobnih sestav. Primerjavo rezultatov ICP analize dveh BCS standardov nikljevih zlitin z atesti prikazujemo v tabeli 3. V tabeli naveden standardni odklik se nanaša na večkratno zaporedno merjenje istega vzorca. Rezultati v glavnem dobro sovpadajo v mejah navedenega standardnega odklika za vse elemente, ra-

chieved for Ni, where the signals of lowest stability were observed. High Cu results were probably caused by high blank value.

The main problem for precise and accurate determination by ICP emission spectrometry, especially for major elements, is maintaining the constant nebulization efficiency and other aparative conditions, wich requires frequent standardisation of calibration curves in short time intervals.

zen za nikelj in baker. Najslabšo ponovljivost in točnost rezultatov smo dobili za nikelj, kjer opazamo najslabšo stabilnost izmerjenih intenzitet. Previsoki rezultati za baker so verjetno posledica sorazmerno visoke slepe vrednosti.

Glavni problem za natančno in točno določanje z ICP AES, predvsem elementov v višjem koncentracijskem območju, je vzdrževanje konstantnih pogojev razprševanja in drugih aparativnih parametrov, kar zahteva večkratno standardizacijo umeritvenih krivulj v kratkih časovnih intervalih.

ZAKLJUČKI

Na osnovi naših opomb, praktičnih izkušenj in dobljenih rezultatov lahko zaključimo, da je predlagana metoda ICP atomske emisijske spektrometrije primerna in perspektivna tehnika za hitro multielementarno analizo večine elementov v preiskovanih nikljevih zlitinah.

CONCLUSIONS

Considering our remarks, practical experiences and results obtained, we can conclude that recommended method by ICP atomic emission spectrometry is an useful, suitable perspective technique for rapid multielement determination for most of major and minor elements in investigated nickel base alloys.

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