

Comparison of Graphite Furnace - and Hydride Generation AAS for Trace Analysis of Tin in Steels and Nickel Alloys

Primerjava elektrotermične - in hidridne tehnike AAS za analizo sledov kositra v jeklih in nikeljevih zlitinah

A. Osojnik, T. Drglin, Inštitut za kovinske materiale in tehnologije, Ljubljana

The determination of tin in various types of steel and nickel superalloys at low concentration level using graphite furnace atomic absorption spectrometry (GF AAS) and batch system hydride generation atomic absorption spectrometry (HG AAS) is described. The analytical and instrumental parameters for both methods were optimized. The interferences of matrix elements and some metalloids were investigated. Certified standard reference materials of steels and nickel alloys were used to test the methods. Some performances and characteristic data (detection limit, characteristic mass, accurate and relative standard deviation) of the two methods are established and compared. The critical estimate of the both methods is performed. Key words: graphite furnace AAS, hydride generation AAS, interferences, steel, nickel alloys, tin determination.

Opisana je metoda ter optimizirani instrumentalni in analizni parametri za določanje sledov kositra v jeklih in nikeljevih zlitinah z metodo elektrotermične atomizacije (GF AAS) in hidridne tehnike-AAS (HG AAS). Študirali smo interference elementov osnove in nekaterih metaloidov. Rezultati so bili preverjeni s certificiranimi referenčnimi materiali jekel in nikeljevih zlitin. Podani so nekateri karakteristični podatki (meja zaznavnosti, karakteristična masa, točnost, relativni standardni odmik) ter primerjava in kritična ocena obeh uporabljenih metod. Ključne besede: elektrotermična AAS, hidridna tehnika AAS, interference, jeklo, nikeljeve zlitine, določanje kositra.

Introduction

Mechanical, physical and technological properties of various types of steel, and especially vacuum cast nickel superalloys for high temperature application strongly depend on trace elements contents such as Bi, Sb, Sn, As, Se, Te, and others. Because of their harmful effect already at the $\mu\text{g g}^{-1}$ levels and lower, the permissible concentrations of these elements are strongly limited, depends upon the element, the alloy type and application purpose. The traces of surface active elements such as Sb, Sn, Se, Te, and others influence the magnetic properties of nonoriented steel sheets. The knowledge of their contents is one of the useful factors for study of segregation phenomena.

Therefore the determination of these elements is extremely important and the development of a suitable, sensitive analytical method is necessary. Graphite furnace - and hydride generation atomic absorption spectrometry seems to be the appropriate techniques for this purpose, because of their sensitivity and relative simplicity.

The main problems in the determination of tin by GF AAS are the formation of volatile Sn compounds, interactions of tin with graphite during the atomization step (1, 2, 3, 4, 5) and matrix interferences (9, 13).

In order to overcome these problems, different chemical modifiers (5, 6, 7, 8), the oxidation of solution with nitric acid (1, 5, 7, 9) and pretreatment of the graphite tubes with refracto-

ry metals (1, 4, 6, 10, 11) and aluminium solution (9) have been suggested. In this way the losses of tin are diminished and efficiency of tin atomization is improved. The use of coated graphite tubes for tin determination has been proposed by many authors (1, 4, 6, 9, 10, 11). This treatment results in the enhancement of sensitivity (1, 4, 6, 7, 9, 10) and reproducibility of signal (9, 10), a reduction of interferences (6, 10), and in the increased life time of the graphite tubes (10). The knowledge and explanation of chemical reactions which occur in graphite furnace during tin determination (1, 2, 12) contribute to better understanding of the actions and the role of metal coatings, matrix modifiers and interfering elements.

Determination of tin by HG AAS has been described by a number of authors (14-20), although many problems exist for this element. It is well known that sensitivity of Sn signal depends strongly on the pH of the sample solution (14, 15, 19). Therefore for tin determination saturated solution of boric acid with addition of low concentrations of nitric (15) or hydrochloric acid (19, 20) for standards, sample and carrier solutions is recommended. Different reagents (acid, sodium tetrahydroborate reductant solution, sodium hydroxide) and their concentrations significantly influence not only sensitivity and peak shapes but also interferences in tin determination by HG AAS. Among the difficulties described in the literature are also high blank values (18, 20, 21), memory effects (20, 21), and interferences from transition metals ions such as Fe, Ni, Co, Cu which cause very

serious reduction of the tin signal (17, 22). The interferences caused by those elements can be partly or completely eliminated. The most common way to eliminate the interferences is masking of interfering ions by different masking agents (17, 22, 23), although the changes of acid and reductant solution concentrations are also useful for this purpose (15, 20). An additional problem in tin determination by HG AAS reported by B. Welz et al. (20) is the appearance of pre-peaks originated from the silica of quartz tube atomizer which can be volatilized and atomized in the presence of hydrogen, most probably via hydrogen radicals. These prepeaks are difficult to separate from the analytical signal and may cause errors in signal evaluation.

The present work involved an extensive study of optimal analytical and instrumental parameters for low level tin determination in steels and nickel alloys using GF AAS and HG AAS. The determination has been discussed regarding:

GF AAS

- influence of graphite tube coatings and modifier used on sensitivity and reproducibility of signal
- interferences of matrix elements
- selection of optimal pyrolysis and atomization temperature with regard to volatilization of analyte, background, interferences, sensitivity of signal and life time of graphite tube
- evaluation of results

HG AAS

- influence of acid concentration on analyte signal
- interferences of matrix elements and some metalloids
- evaluation of results

Experimental

Aparatus

The GBC 902 atomic absorption spectrometer, equipped with deuterium-arc background correction system, automated graphite furnace GF 2000, programmable auto-sampler PAL 2000 and CL 2000 controller was used for the measurements of analyte absorbances using GF AAS. The instrumental parameters and operating conditions are given in **Table 1**. The furnace program is shown in **Table 2**.

A Perkin-Elmer 2380 atomic absorption spectrometer, equipped with hydride generator MHS-10 and printer PRS-10 was used for hydride generation and absorbances measurements using HG AAS. The instrumental parameters and operating conditions are listed in **Table 3**.

Table 1: Instrumental parameters and operating conditions for GF-AAS

Spectrometer	GBC, double beam, 902
Wavelength	286.3 nm
Slit	1.0 nm
Light source	HCL, 10 mA
Measurement mode	peak height
Furnace	
Graphite tube	coated with Na ₂ WO ₄
Char temperature	800°C
Atomization temp.	2600°C
Sampler	
Sample volume	20 µl
Standard preparation	
Stock solution	1000 µg/ml Sn in 1 M HCl
Standard solutions	serial dilutions with 0.3 M HNO ₃
Sample preparation	
Dissolved in	20 ml aqua regia
Mass/volume	0.5 g/50 - 1 to 10/100 ml (diluted with 0.3 M HNO ₃)

Table 2: Graphite furnace temperature program for the determination of tin in steels and nickel alloys

Step number	Temp. (°C)	Ramp time (s)	Hold time (s)	Ar flow (l min ⁻¹)
1	90	1	9	1.3
2	120	10	10	1.3
3	80	10	10	1.3
4	800	1	1	-
5	2600	1	3	-
6	2650	1	6	1.3
7	20	1	5	1.3

Table 3: Instrumental parameters and operating conditions for HG-AAS

Spectrometer	Perkin-Elmer, 2380
Wavelength	286.3 nm
Slit	0.7 nm
Light source	EDL, 6 W
Hydride system	Perkin-Elmer, MHS-10
Stock solution	1000 µg/ml Sn (in 1 M HCl)
Standard solutions	serial dilutions with 0.1 M HCl
Carrier solution	H ₃ BO ₃ , sat./0.1 M HNO ₃
Calibration volume	25 ml
Reductant	3 g NaBH ₄ + 0.5 g NaOH/100 ml
Flame	air/acetylene: blue
Sample	
Dissolved in	20 ml aqua regia
Mass/volume	0.5 g/50 ml
Measuring volume	0.1-1.0 ml
Elimination of interferences	3 g sodium oxalate/100 ml

Reagents

All reagents were of highest available purity (p.a. or puriss. p.a.) obtained from Merck or Fluka. The solutions prepared were:

GF AAS

- aqua regia
- nitric acid, 0.3 M
- Pd/Mg nitrate modifier: 300 mg Pd (dissolved in nitric acid) + 200 mg Mg(NO₃)₂ · 6H₂O in 100 ml of water
- sodium tungstate dihydrate, 5 g in 100 ml of water

HG AAS

- aqua regia
- carrier solution: saturated boric acid containing 0.1 M nitric acid
- reduction solution: 3 g of sodium tetrahydroborate (Fluka) in 100 ml of water stabilised with 0.5 g of sodium hydroxide
- sodium oxalate, 3 g in 100 ml of water

Standard solutions

Stock solution of 1000 µg ml⁻¹ Sn was prepared by dissolving of 1.000 g of tin metal in 100 ml hydrochloric acid (1.16) and diluting to 1 l with deionized water. The other standard solutions were prepared from stock solution by serial dilution with 0.3 M nitric acid for GF AAS or with 0.1 M hydrochloric acid for HG AAS. Standard Sn solutions containing the interfering ions were prepared by adding the appropriate amounts of interfering ions to the standard solutions.

Sample preparation

0.5 g of sample was carefully dissolved in 20 ml of aqua regia (2 hours at 90°C). After cooling the digest was diluted to 50 ml with deionized water. Further dilution of sample solution (10-100 times) with 0.3 M nitric acid was used for GF AAS measurements.

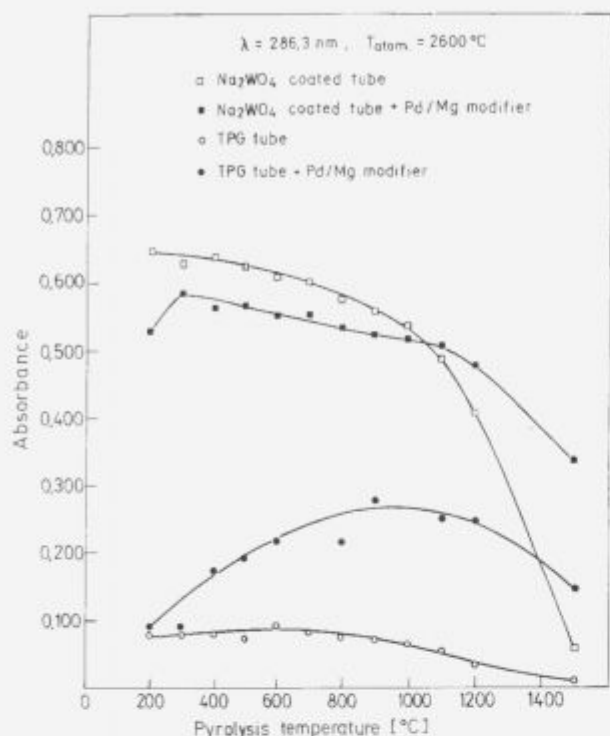


Figure 1: Effect of graphite tube coating and matrix modifier on signal for 2 ng Sn at different pyrolysis temperatures

Slika 1: Vpliv prevleke grafitnih cevki in modifikatorja na signal za 2 ng Sn pri različnih razkrojnih temperaturah

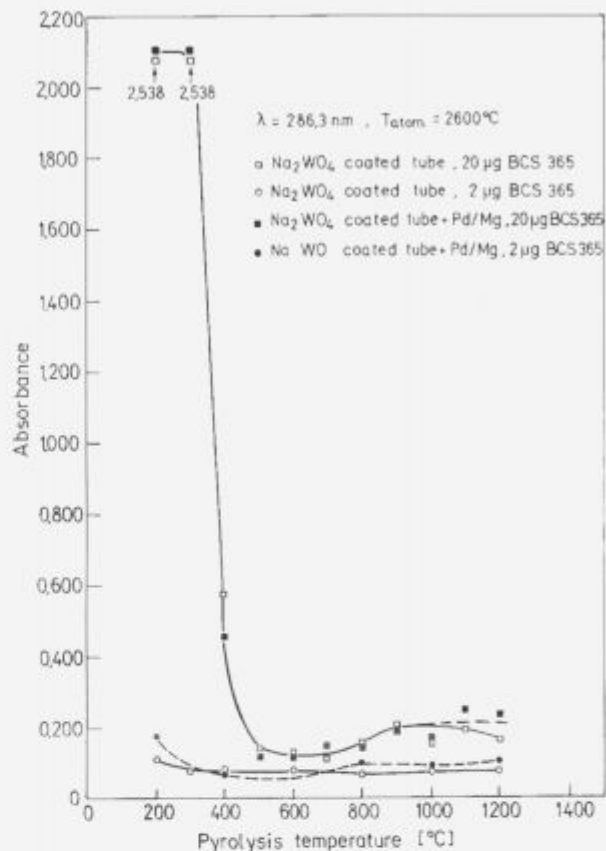


Figure 3: Determination of background for Sn in steel vs. pyrolysis temperature

Slika 3: Določanje ozadja za Sn v jeklih v odvisnosti od razkrojne temperature

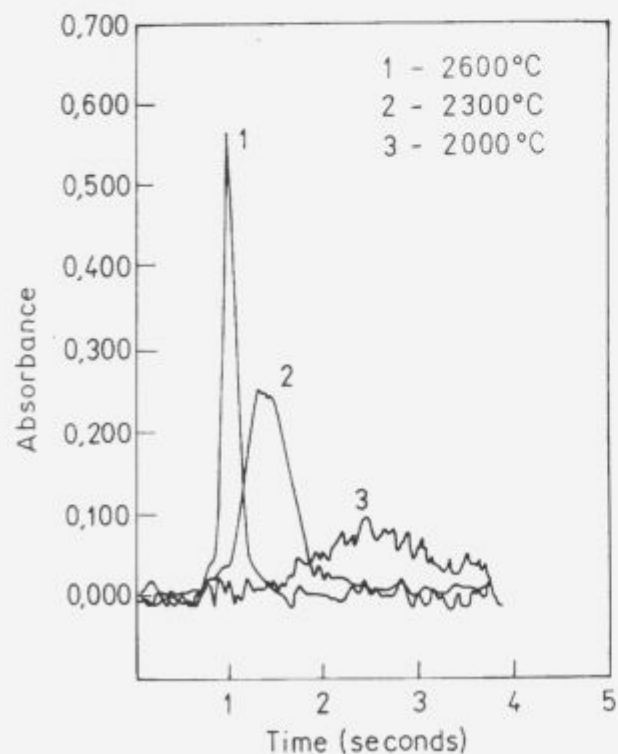


Figure 2: Effect of atomization temperature on signal for 2 ng Sn

Slika 2: Vpliv temperature atomizacije na signal za 2 ng Sn

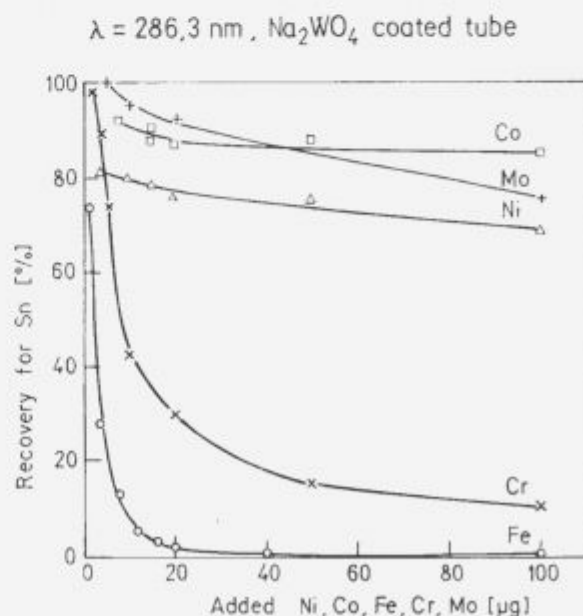


Figure 4: Influence of interferent elements on the signal for 2 ng Sn: GF AAS

Slika 4: Vpliv motečih elementov na signal za 2 ng Sn: GF AAS

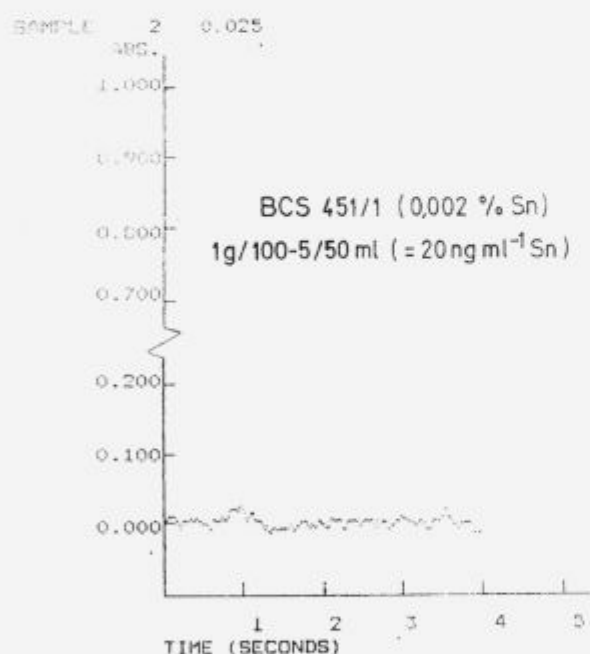
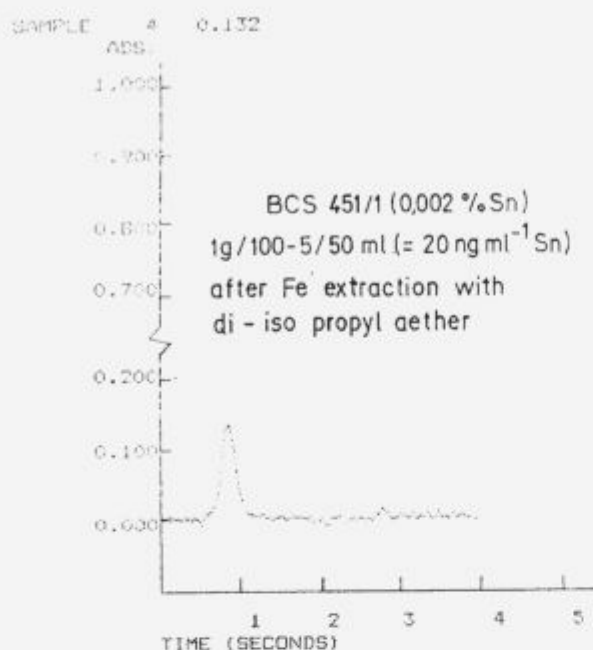


Figure 5: Effect of Fe extraction from steel on Sn-signal by GF AAS
Slika 5: Vpliv ekstrakcije železa iz jekla na Sn signal z metodo GF AAS

Pretreatment of graphite tube⁽²⁴⁾

The graphite tube was soaked with sodium tungstate solution for 8 hours, than the tube was dried at 120°C and heated in the furnace tube under the conditions shown in Table 4. The whole procedure was repeated once more.

Table 4: Furnace conditions for W carbide coating

Step number	Temp. (°C)	Ramp time (s)	Hold time (s)	Ar flow (l min ⁻¹)
1	120	10	60	1.3
2	2600	90	10	—
3	2900	10	10	1.3

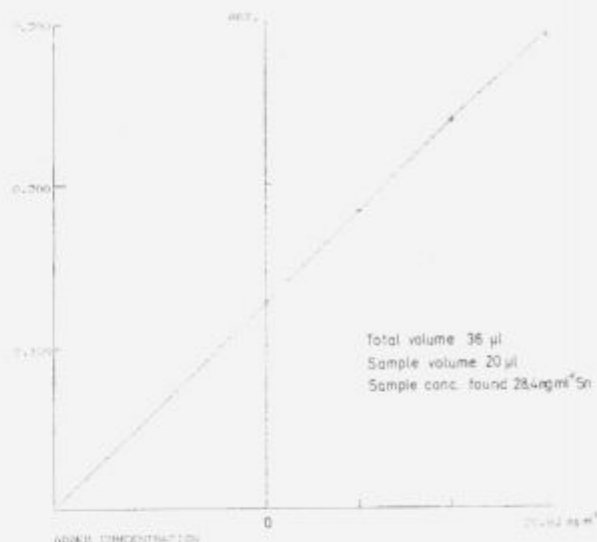


Figure 6: Standard addition method for the determination of Sn in steel by GF AAS

Slika 6: Metoda standardnega dodatka za določanje Sn v jeklih z metodo GF AAS

Calibration

The calibration curve made by standard addition method was applied using GF AAS.

For HG AAS calibration was carried out with standard solutions in the range from 10 to 100 ng Sn, matched with corresponding amounts of matrix elements.

Results and Discussion

The results of the work carried out with the intention of optimizing instrumental and analytical parameters for tin determination in steels and nickel alloys using GF AAS and HG AAS are shown in following figures.

Effect of graphite tube coating and matrix modifier on sensitivity of Sn signal at different pyrolysis temperatures is demonstrated in figure 1. The W-coated graphite tube shows the largest increase in sensitivity among the coatings used (W-, Ta-, Zr-coatings). It is evident that pyrolysis can be done at temperatures up to 1000°C without greater loss of Sn. The matrix modifier proposed by Schlemmer and Welz⁵ (Pd/Mg nitrate modifier) has essentially no influence on the absorbance signal of tin at this tem-

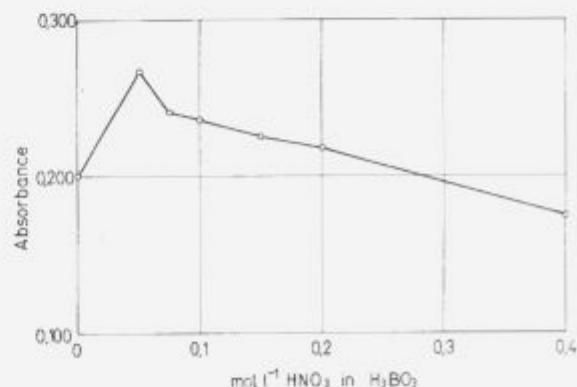


Figure 7: Influence of nitric acid concentration on Sn signal using HG AAS

Slika 7: Vpliv koncentracije dušikove (V) kisline na Sn signal z metodo HG AAS

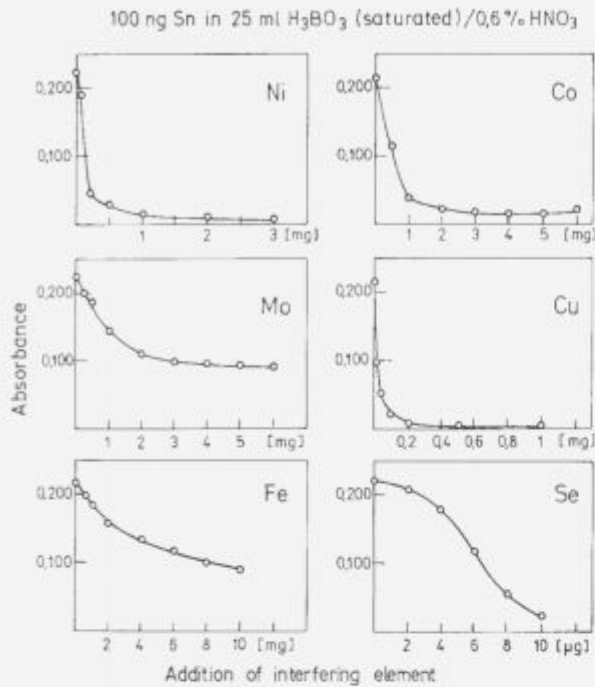


Figure 8: Influence of the interfering elements on signal for Sn by HG AAS

Slika 8: Vpliv motečih elementov na Sn signal z metodo HG AAS

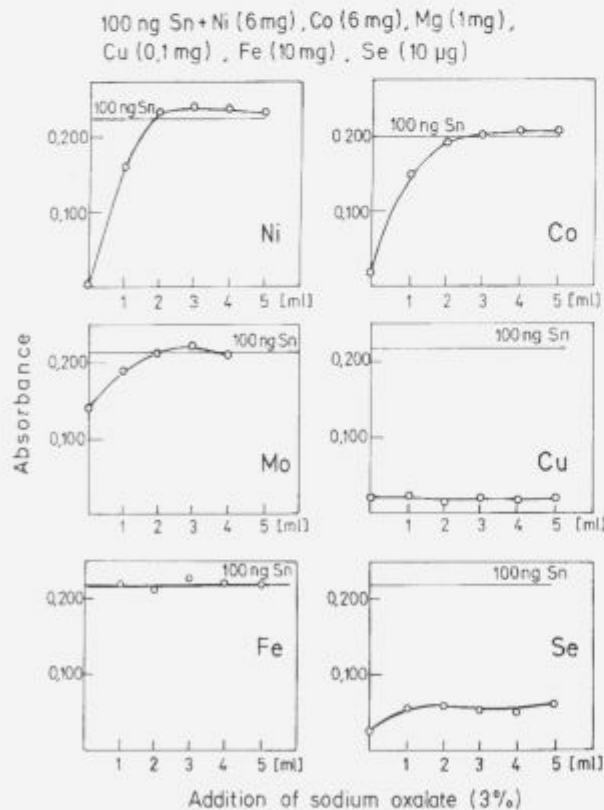


Figure 9: Elimination of interferences for Sn with the addition of sodium oxalate (HG AAS)

Slika 9: Eliminiranje motenj za Sn z dodatkom natrijevega oksalata (HG AAS)

perature. The sensitivity increase due to matrix modifier action is observed only at pyrolysis temperatures above 1200°C.

Effect of atomization temperature on Sn signal is shown in figure 2. The efficiency of tin atomization is improved at atomization temperature 2600°C.

The absorbance signal of background in dependence of pyrolysis temperature for Sn determination in steel samples is presented in figure 3. For sample amount of 20 µg the background is reduced on acceptable value at pyrolysis temperature above 500°C.

The interfering effect of matrix elements on signal of Sn is shown on figure 4. As indicated the presence of Fe and Cr depress the Sn signal strongly. Since it was confirmed (13, 15) that the extent of the interferences by the transition metal ions does not depend on the analyte - interferent ratio, but on the interferent concentration in the sample solution, larger matrix dilution for high Sn contents can be used to reduce these interferences.

In the case that Sn concentration in the sample is very low a prior separation (MIBK extraction) of interfering iron must be done. The depressing effect of iron on Sn signal can be seen from figure 5, where the comparison of peaks resulting from tin determination with and without the iron separation is shown. For tin determination in steels the dilution of sample is recommended. The absorbance signal for diluted steel sample is namely greater as for undiluted sample, although the tin amount for diluted sample is absolutely smaller. Therefore the evaluation of results has to be performed by the calibration curve made by the standard addition method which is demonstrated in figure 6.

The following figures present the results of our experiments made with intention of optimizing the analytical parameters for tin determination using HG AAS. The influence of nitric acid concentration in the carrier solution on sensitivity for tin is confirmed (figure 7). As reported (15, 19) the addition of low concentration of nitric acid to the saturated boric acid improves the sensitivity and reproducibility of Sn signal.

The influence of interfering elements on Sn signal by HG AAS is shown in figure 8. The presence of Ni, Fe, Co, Cu, Mo and Se depress the signal for Sn strongly.

The interfering effect of Ni, Fe, Co and Mo is eliminated by addition of sodium oxalate (figure 9), although a number of masking agents were examined. The interference of Se is stated only in concentrations much higher than in samples investigated.

Certified reference standard materials of steels and nickel alloys were used to test the methods. Certified values for Sn concentrations in standards used are collected in table 5. The comparison results of Sn determination in steel and nickel alloys are given in table 6. The results indicated a good agreement with certified values for both methods within the reported standard deviation, although the reproducibility of results is better by GF AAS.

Table 5: Certified reference standard materials used for Sn determination

Sign	Material	Atest µg g ⁻¹ Sn
BCS 239/3	0.3 % carbon steel	300
BCS 433	plain carbon steel	100
BCS-CRM 451/1	carbon steel	20
EURO-CRM 281-1	highly alloyed steel	90
EURONORM ZRM 285-1	highly alloyed steel	30
BCS-CRM 345	IN 100 alloy	6
BCS-SRM 346	IN 100 alloy	91
MBH 11982 B	nickel alloy IN 100	88
MBH 11980 F	nickel alloy IN 100	18

Table 6: Comparison of GF-AAS and HG-AAS results ($\mu\text{g g}^{-1}\text{Sn}$) with certified values

Certified references samples	Certified value	GF-AAS		HG-AAS	
		found	\pm RSD	found	\pm RSD
BCS 345	6 \pm 1.6	4.9	\pm 15.2 %	4.9	\pm 18.0%
BCS 345+10 $\mu\text{g g}^{-1}\text{Sn}$	16	15.8			
BCS 346	91 \pm 7	94.2	\pm 7.3	96.0	\pm 7.5%
MBH 11980	18	15.1 \pm	15.1 %	19.0	\pm 11.0%
MBH 11982	88	76.3	\pm 8.7 %	81.2	\pm 8.2 %
BCS 239/3	300(280-330)	320	\pm 1.7 %	309	\pm 5.0 %
BCS 433	100(80-110)	93	\pm 3.5 %	93	\pm 8.3%
BCS 451/1	20(13-23)	18	\pm 5.9 %	15	\pm 9.2 %
EURO-CRM 281-1	90 \pm 10	102	\pm 3.3 %	97	\pm 4.1%
EURO-ZRM 285-1	30 \pm 8	33	\pm 6.8 %	26	\pm 8.4 %

Some characteristic data of both methods used are collected in **table 7**. The calculated values are nearly in a good agreement with available reported data. The sensitivity (characteristic mass) of GF AAS method is better as for HG AAS, which is compensated with greater measuring volume by HG AAS. Interesting is the difference in the characteristic mass calculated from analysis results of diluted and undiluted samples which is the consequence of depressing effect of interfering elements.

Table 7: Characteristic data for method evaluation (detection limit, characteristic mass)

Method	Sample	Dilution	Measuring volume	DL ng ml ⁻¹	$\mu\text{g g}^{-1}$	m_0 pg
GF-AAS	standard solution		20 μl	1.2		17.1
GF-AAS	BCS 345	1g/100 ml	20 μl	5.4	0.54	79.1
GF-AAS	BCS 346	1g/100-10/50 ml	20 μl	3.7	1.84	27.0
GF-AAS	BCS 239/3	0.5g/50-10/100 ml	20 μl	7.2	7.2	106
GF-AAS	BCS 239/3	0.5g/50-1/50 ml	20 μl	1.3	1.7	17.9
GF-AAS	BCS 281/1	0.5g/50-10/100 ml	20 μl	2.5	2.5	36
GF-AAS	BCS 281-1	0.5g/50-1/100 ml	20 μl	0.7	7.3	10.7
HG-AAS	standard solution		1 ml	2.7		1982
HG-AAS	BCS 345	1g/100 ml	1 ml	3.3	0.33	2440
HG-AAS	BCS 346	1g/100-10/100 ml	1 ml	2.7	2.7	2010
HG-AAS	BCS 239/3	0.5g/50 ml	0.05 ml	2.1	4.2	1941
HG-AAS	BCS 451/1	1g/100 ml	0.1 ml	2.7	2.7	2514
HG-AAS	BCS 451/1	1g/100 ml	0.5 ml	3.2	0.64	2933

Conclusions

The W-coated graphite tubes was chosen to improve the sensitivity and reproducibility of Sn signal by GF AAS. The strongly interfering effect of iron and chromium was stated at analyses conditions used. Dilution of samples for high Sn contents or prior iron separation for steel samples in low concentration levels ($<20 \mu\text{g g}^{-1}$) is the only way to overcome this problem. The evaluation of results has to be performed by the calibration curve made by standard addition method.

The interferences of Ni, Fe, Co, Cu and Mo, due to preferential reduction of interfering elements to elementary state and kinetic changes of hydride forming reactions were established

using HG AAS. The interferences of hydride forming elements (Se) were stated only in concentrations much higher than in samples investigated. The interfering effect of Ni, Fe, Co and Mo is eliminated by addition of sodium oxalate.

Certified reference standards of steels containing 20-300 $\mu\text{g g}^{-1}$ Sn and nickel alloys containing 6-91 $\mu\text{g g}^{-1}$ Sn were used to test the methods. Characteristic mass is lower by GF AAS. This can be compensated with greater measuring volume by HG AAS. Reproducibility of results is in the range of ± 2 to $\pm 15\%$ for GF AAS and ± 4 to $\pm 18\%$ for HG AAS. The accuracy of results are in agreement with certified values within the reported standard deviation for the both methods.

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