Trace Element Analysis of Steels and Nickel Alloys by Atomic Spectrometry

A. Osojnik, M. Renko, T. Drglin, Z. Torkar

► To cite this version:

A. Osojnik, M. Renko, T. Drglin, Z. Torkar. Trace Element Analysis of Steels and Nickel Alloys by Atomic Spectrometry. Journal de Physique IV Proceedings, 1995, 05 (C7), pp.C7-189-C7-197. 10.1051/jp4:1995720 . jpa-00254013

HAL Id: jpa-00254013

<https://hal.science/jpa-00254013>

Submitted on 1 Jan 1995

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Trace Element Analysis of Steels and Nickel Alloys by Atomic Spectrometry

A. Osojnik, M. Renko, T. Drglin and Z. Torkar

Institute of Metals and Technology, Ljubljana, Slovenia

Abstract. The determination of arsenic and antimony in electrical steel sheets and nickel-base alloys at low concentration levels using graphite furnace atomic absorption spectrometry was investigated. The analytical and instrumental parameters were optimized. The influence of various modifiers on sensitivity and reproducibility of analytical signal was studied. The selection of optimal temperature program with regard to volatilization of the elements under investigation, background, matrix interferences, sensitivity and reproducibility of analytical signal and the life time of graphite tube was made. Some characteristic data, such as detection limit, characteristic mass and reproducibility of results were determined. The accuracy of the method was tested with certified standard reference materials of steels and nickel alloys. The experimental results agreed closely with the certified values for the both elements.

1. INTRODUCTION

Mechanical properties of various types of steel, and especially vacuum cast nickel super-alloys for high temperature application strongly depend on the presence of trace volatile elements, such as Ag, As, Bi, Pb, Sb, Se, Sn, 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 strictly limited and depend upon the element, the alloy type and application purpose. The traces of surface active elements such as As, Sb, Se, Sn, Te and others influence the magnetic properties of non-oriented steel sheets. The knowledge of their contents is one of the useful items of information for the study of segregation phenomena.

The determination of trace levels of these elements is therefore extremely important, and the development of a suitable, sensitive method is necessary. Since the technique of graphite furnace atomic absorption spectrometry (GF AAS) has evolved, lower detection limits have been obtained and its application seems to be appropriate for above-mentioned purpose.

The main problems in measurement by GF AAS are the formation of volatile compounds, interactions of some elements with graphite during the atomization step, non specific background absorption and matrix interferences. In order to overcome these problems, improved background correction [1,2], the use of different chemical modifiers [1,3,4,5,6,18,19,21,22,23,24] and pre-treatment of the graphite tubes [1,8,9,10,11,12,13] have been suggested. In this way the losses of volatile elements are diminished and the efficiency of atomization is improved.

The progress made in instrumentation over the past decade has brought substantial improvements in GF AAS methodology [14]. Another step forward has been the freedom from interference achieved with the

stabilised temperature platform furnace (STPF) concept proposed by Slavin and co-workers [15,16,17]. These conditions allow calibration against matrix-free reference solutions when integrated absorbance is used for evaluation of the absorption pulse [6].

All these findings have resulted in a great deal of analytical work to evaluate their applicability to a variety of analytical applications.

The present work involved an extensive study of optimal analytical and instrumental parameters for low level arsenic and antimony determination in steel and nickel-base alloys using GF AAS.

2. EXPERIMENTAL

2.1 Apparatus

The GBC 902 atomic absorption spectrometer, equipped with a deuterium-arc background correction system, a GF 2000 automated graphite furnace, a PAL 2000 programmable auto-sampler and a CL 2000 controller were used for the measurements of absorbance of the substances under investigation using GF AAS. The instrumental parameters and operating conditions are given in Table 1. The temperature furnace program for As and Sb determination are shown in Table 2 and Table 3.

	As	Sb
Wavelength	193.7 nm	217.6 nm
Slit	0.7 nm	0.7 nm
Light source	EDL, 7 W	EDL, 7 W
Measurement mode	peak height	
Graphite tube	pyrolytically coated	
Chemical modifier	Pd/Mg nitrate	
Modifier volume	10 μ l	10 μ l
Sample volume	20 μ l	20 μ l

Table 1. Instrumental parameters and operating conditions

Step number	Final temp. (°C)	Ramp time (s)	Hold time (s)	Ar flow (l min ⁻¹)
1	90	1	10	1.3
2	120	10	20	1.3
3	800	10	20	1.3
4	800	1	0.1	-
5	2500	1	6	-
6	2650	1	5	1.3

Table 2. Graphite furnace temperature program for As determination

Step number	Final temp. (°C)	Ramp time (s)	Hold time (s)	Ar flow (l min ⁻¹)
1	90	1	10	1.3
2	120	10	20	1.3
3	1000	10	20	1.3
4	1000	1	0.1	-
5	2500	1	6	-
6	2650	1	5	1.3

Table 3. Graphite furnace temperature program for Sb determination

2.2 Reagents

All reagents were of highest available purity (p.a. or puriss. p.a.) from Merck or Fluka.

- Pd/Mg nitrate modifier was prepared by mixing equal volumes of a solution containing 300 mg/100 ml of palladium (dissolved in nitric acid) and 200 mg/100 ml of $\text{Mg}(\text{NO}_3)_2$
- Ni modifier was prepared by dissolving 4.03 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 2 ml of concentrated nitric acid, evaporating till dryness and diluting with de-ionised water to 100 ml.

2.3 Standard solutions

- Stock solution of 1000 $\mu\text{g ml}^{-1}$ As was prepared by dissolving 1.3203 g of arsenic (III) oxide with a minimum volume of 20 % NaOH, neutralizing with nitric acid and diluting to 1000 ml. Reference solutions were prepared daily by diluting the stock standard solution with 2 % nitric acid.
- Stock solution of 1000 $\mu\text{g ml}^{-1}$ Sb was prepared by dissolving 1000 g of antimony in 100 ml hydrochloric acid containing 2 ml nitric acid and diluting to 1000 ml. Reference solutions were prepared daily from stock solution by serial dilutions with 2 % nitric acid.

2.4 Sample preparation

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

2.5 Calibration

Calibration was performed by the standard addition method.

3. RESULTS AND DISCUSSION

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

The effect of matrix modifiers on the Sb signal at different char (pyrolysis) temperatures is demonstrated in figure 1. The Pd/Mg nitrate matrix modifier proposed by Schlemmer and Welz [4] allows the use of higher pyrolysis temperatures without greater loss of antimony. It is evident that pyrolysis can be performed up to 1000°C for Sb and 800°C for As in the presence of Pd/Mg modifier.

The effect of matrix modifiers on the Sb signal at different char (pyrolysis) temperatures is demonstrated in figure 1. The Pd/Mg nitrate matrix modifier proposed by Schlemmer and Welz [4] allows the use of higher pyrolysis temperatures without greater loss of antimony. It is evident that pyrolysis can be performed up to 1000°C for Sb and 800°C for As in the presence of Pd/Mg modifier.

Figure 1. Effect of matrix modifier on signal for 2 ng Sb at different char temperatures

The influence of atomization temperature on Sb signal in the presence of different matrix modifiers is shown in Figure 2. The efficiency of Sb atomization is improved at atomization temperature 2500°C in the presence of Pd/Mg nitrate modifier. The Ni nitrate modifier has no influence on the absorbance signal of antimony at this temperature.

Figure 2. Influence of atomization temperature on signal for 2 ng Sb in the presence of different matrix modifiers

The efficiency of arsenic atomization is improved at atomization temperature 2500°C in the presence of Pd/Mg nitrate modifier. The effect of atomization temperature on the arsenic peak shape can be seen from Figure 3.

Figure 3. Effect of atomization temperature on the peak shape for 2 ng As

The influence of interfering elements on the analysis signal is shown in figure 4 (As) and figure 5 (Sb). The strong interfering effect of iron, nickel, cobalt, chromium and to a lesser degree titanium and molybdenum (for Sb determination) was observed under the analysis conditions used.

Figure 4. Influence of interfering elements on the signal for 2 ng As

Figure 5. Influence of interfering elements on the signal for 2 ng Sb

Since it has been confirmed [25] that the extent of the interference by the transition metal ions does not depend on the ratio of elements studied to interferent, but on the interferent concentration in the sample solution, higher matrix dilutions can be used to reduce this interference. The dilution of the samples is recommended. This is because the absorbance signal for a diluted sample is greater than for undiluted, although the amount of element under study in a diluted sample is smaller in absolute terms. The evaluation of results has to be performed by the calibration curve made by the standard addition method which is demonstrated in Figure 6.

Figure 6. Standard addition method for determination of Sb in steel

Certified standard reference materials of steels and nickel alloys were used to test the method. Certified values for As and Sb concentrations in the standards used are summarized in table 4.

Sign	Material	Atest	
		$\mu\text{g g}^{-1}$ Sb	$\mu\text{g g}^{-1}$ As
BCS 460/1	Carbon steel	38 ± 4	-
NBS 363	Low-alloy steel	20	100
ZRM 285-1	Hoch legierter stahl	6 ± 2	120 ± 20
BCS-CRM 346	IN 100 alloy	47 ± 3	50 ± 2
MBH 11982 B	IN 100 Alloy	< 0.3	25
BCS/SS-CRM 387/1	NIMONIC 901 alloy	3 ± 1	-

Table 4. Certified reference standard materials used for Sb and As determination

The comparison results of Sb and As determination in steel and nickel alloy are given in Table 5. The results obtained show good agreement and reproducibility for both elements.

Certified reference standard material	Certified value		Concentration found	
	$\mu\text{g g}^{-1}$ Sb	$\mu\text{g g}^{-1}$ As	$\mu\text{g g}^{-1}$ Sb	$\mu\text{g g}^{-1}$ As
BCS 460/1	38 ± 4	-	33 ± 2	-
NBS 363	20	100	22 ± 2	96 ± 8
ZRM 285-1	6 ± 2	120 ± 20	8 ± 3	112 ± 10
BCS-CRM 346	47 ± 3	50 ± 2	45 ± 6	46 ± 5
MBH 1198 2 B	< 0.3	25	< 1	24 ± 4
BCS/SS-CRM 387/1	3 ± 1	-	2 ± 1	-

Table 5. Comparison of GF AAS results with certified values

Some characteristic data are summarized in Table 6.

Sample	Dilution	Measur. vol μl	Elem.	Detect. limit		Char. mass pg
				ng ml^{-1}	mg g^{-1}	
Standard solution		20	Sb	1.6	-	16.3
NBS 363	0.5g/50ml	20	Sb	5.4	0.5	54.7
NBS 363	0.5g/50-5/50ml	20	Sb	2.5	2.5	25.5
BCS 387/1	0.5g/50ml	20	Sb	3.9	0.4	39.4
BCS 387/1	0.5g/50-20/25ml	20	Sb	3.6	0.9	36.4
Standard solution		20	As	1.3	-	10.9
NBS 363	0.5g/50ml	20	As	9.9	1.0	82.9
NBS 363	0.5g/50-5/50ml	20	As	2.2	2.2	18.3
BCS 346	0.5g/50ml	20	As	5.9	0.6	49.6
BCS 346	0.5g/50-5/50ml	20	As	1.6	1.6	13.1

Table 6. Characteristic data for method evaluation

The detection limit is about 0.5 to 2 $\mu\text{g g}^{-1}$, depending on the weight and dilution of the sample. It is interesting to note the difference in the characteristic mass calculated from analysis results of diluted and undiluted samples, which is a consequence of the depressing effect of interfering elements.

4. CONCLUSIONS

Pd/Mg nitrate matrix modifier was chosen to prevent the loss of Sb and As during charring and to minimize the interfering effect of some elements before atomization.

The strong interfering effect of iron, nickel, cobalt, chromium and to a lesser degree of titanium and molybdenum (for Sb determination) was observed under the analysis conditions used. Dilution of samples is the only way to overcome this problem. The evaluation of results has to be performed by the calibration curve made by the standard addition method.

Certified standard reference materials of steels and nickel alloys containing 3-47 $\mu\text{g g}^{-1}$ Sb and 20-120 $\mu\text{g g}^{-1}$ As were used to test the method. The results obtained show good agreement and reproducibility for both elements.

References

- [1] Pruszkowska E., Manning D. C., Carnick G. R. and Slavin W., *At. spectrosc.* 4(1983) 87
- [2] Martinsen I., Radzink B. and Thomassen Y., *J. Anal. At. Spectrom.* 3(1988) 1013
- [3] Hocquellet P. and Labeirie N., *At. Absorpt. Newsl.* 16(1977) 124
- [4] Schlemmer G. and Welz B., *Spectrochim. Acta* 4B(1986) 1157
- [5] Welz B., Schlemmer G. and Mudakavi J. R., *J. Anal. At. Spectrom.* 3(1988) 93
- [6] Welz B., Schlemmer G. and Mudakavi J. R., *J. Anal. At. Spectrom.* 3(1988) 695
- [7] Bermejo-Barrera P., Soto-Ferreiro R. M. and Bermejo-Barrera A., *Fresenius J. Anal. Chem.* 345(1993) 60
- [8] Iwamoto E., Shimazu H., Jokota K. and Kumamaru T., *J. Anal. At. Spectrom.* 7(1992) 421
- [9] Gruner K., *Neue Hutte* 36(1991) 33
- [10] Fritzsche H., Wegsnider W. and Knapp G., *Talanta* 26(1979) 219
- [11] Hocquellet P., *At. Spectrosc.* 6(1985) 69
- [12] Welz B., Schlemmer G. and Voellkopf U., *Spectrochim. Acta* 39B(1984) 501
- [13] Ortner H. M., Kantuscher F., *Talanta* 22(1975) 581
- [14] Wendl W., Muller-Vogt G. and Hahn I., *Fresenius J. Anal. chem.* 333(1989) 763
- [15] Slavin W., Manning D. C. and Carnick G. R., *At. Spectrosc.* 2(1981) 137
- [16] Slavin W. and Manning D. C., *Spectrochim. Acta* 37(1982) 955
- [17] L'vov B. V., *J. Anal. At. Spectrom.* 3(1988) 9
- [18] Suh-Jen J. T., Ching-Ching J. and Li-Lin C., *Spectrochim. Acta* 49B(1994) 773
- [19] Voth-Beach L. M. and Shrader D. E., *J. Anal. At. Spectrom.* 2(1987) 45
- [20] Guevremont R., *Anal. Chem.* 51(1980) 1574
- [21] Benart H. and Pinta M., *At. Spectrosc.* 3(1982) 8
- [22] Gladney E. S., *At. Absorpt. Newsl.* 16(1977) 114
- [23] Stein V. B., Canelli E. and Richards A. M., *At. Spectrosc.* 1(1980) 61
- [24] Stein V. B., Canelli E. and Richards A. H., *At. Spectrosc.* 1(1980) 133
- [25] Welz B. and Melcher M., *Spectrochim. Acta* 36B(1981) 439