JOURNAL OF ENGINEERING annals OF FACULTY OF ENGINEERING HUNEDOARA
Tome V (year 2007), Fascicole 3, (ISSN 1584 – 2673)

THE USE A SINGLE SPECIFIC STANDARD FOR THE DETERMINATION OF CHEMICAL COMPOSITION OF COBALT – BASE ALLOYS BY ATOMIC ABSORPTION SPECTROMETRY METHOD

WYCIŚLIK Andrzej

SILESIAN UNIVERSITY OF TECHNOLOGY, FACULTY OF MATERIALS SCIENCE AND METALLURGY, KATOWICE, POLAND

ABSTRACT:
A flame atomic absorption procedure has been developed for the analysis of cobalt – base alloys. The samples are dissolved in hydrochloric and nitric acids. To compensate the influences of matrix the analytical curves were obtained the "single specific standard" method. It is based on the use of different weighed amounts of the standard, to which after or during dissolution a given amount of the main element is introduced to equalize its content in standards and samples analysed at the same level, compensating at the same time their influence on the determined element. The precision and accuracy of the proposed method were determined by replicate analysis of samples or values obtained by wet chemical analysis. The precision was as follows: Cr 1.08 – 1.38 %, Ni 0.95 – 1.25 %, Mo 1.09 – 1.31 %, Al 1.09 – 1.22 %, Mn 0.81 – 1.08 %, Fe 1.79 – 2.65 % and Cu 1.36 – 1.66 %.
KEYWORDS:
cobalt alloys, atomic absorption spectrometry, single specific standard

1. INTRODUCTION

Cobalt-base alloys have not less complex chemical composition than nickel alloys, especially high-temperature nickel-base alloys (2,5). To determine its contents of metallic elements in cobalt alloys the atomic absorption spectrometry (AAS) method has been used in recent years, because of its main advantages, i.e. a high sensitivity, selectivity and precision (3,6,8,12). Usually three to ten metallic elements are being determined in cobalt alloys. The determination of the chemical composition of cobalt alloys, in this work, was concentrated on cobalt alloys applied in medicine for implantation materials. These alloys contain the following elements: chromium 10-50 %, nickel 0-6 % and 10-30 %, manganese 0-2 %, molybdenum 0-10 %, iron 0-8 % and 10-40 %, aluminium 0-3 % and copper 0-0.5 %. Taking into account the numerous interelement interactions it has been decided, instead of preparing series of synthetic standard solutions, to use the previously reported method of calibration using a single specific standard (10,11). This method consists in using of various weighed amounts of one specific (initial) standard to which after or during digestion appropriate amounts of the main component of the matrix are introduced to equalise its contents in standards and in analysed samples to a similar, within some tolerance, level balancing its influence on the element being determined.

2. APPARATUS AND REAGENTS

Determination of the elemental contents in cobalt-base alloys was carried out by atomic absorption spectrometry using a Perkin-Elmer Model 603 spectrometer. Perkin-Elmer Intensitron hollow cathode lamps were used as radiation sources. During the determination of individual elements initial pressures and gas flows were used as in the manufacturer's manual, however, each time the gas flows were regulated in such a way as to obtain the maximum stable reading of absorbance (13). Detailed operating parameters have been specified in Table 1. The analytical procedure is summarized in Figure 1.

TABLE 1. Operating parameters

Element	Wavelength, nm	Slit, nm	Flame	Type of flame 1)	Burner height, mm	Linear working range, µg/ml
Cr	357.9	0.7	C_2H_2 - N_2O	R	9	10
Ni	232.0 341.5	0.2 0.2	C_2H_2 – Air	O	5	10 25
Mo	313.3 317.0	0.7 0.7	C_2H_2 - N_2O	R	8	60 80
Al.	309.3 394.4	0.7 0.7	C_2H_2 - N_2O	R	5	60 120
Mn	279.5 403.1	0.2 0.2	C_2H_2 – Air	O	4	4 25
Fe	248.3 372.0	0.2 0.2	C_2H_2 – Air	O	6	5 60
Cu	324.7 327.4	0.7 0.7	C_2H_2 – Air	O	4	5 25

1) O – oxidizing, R – reducing

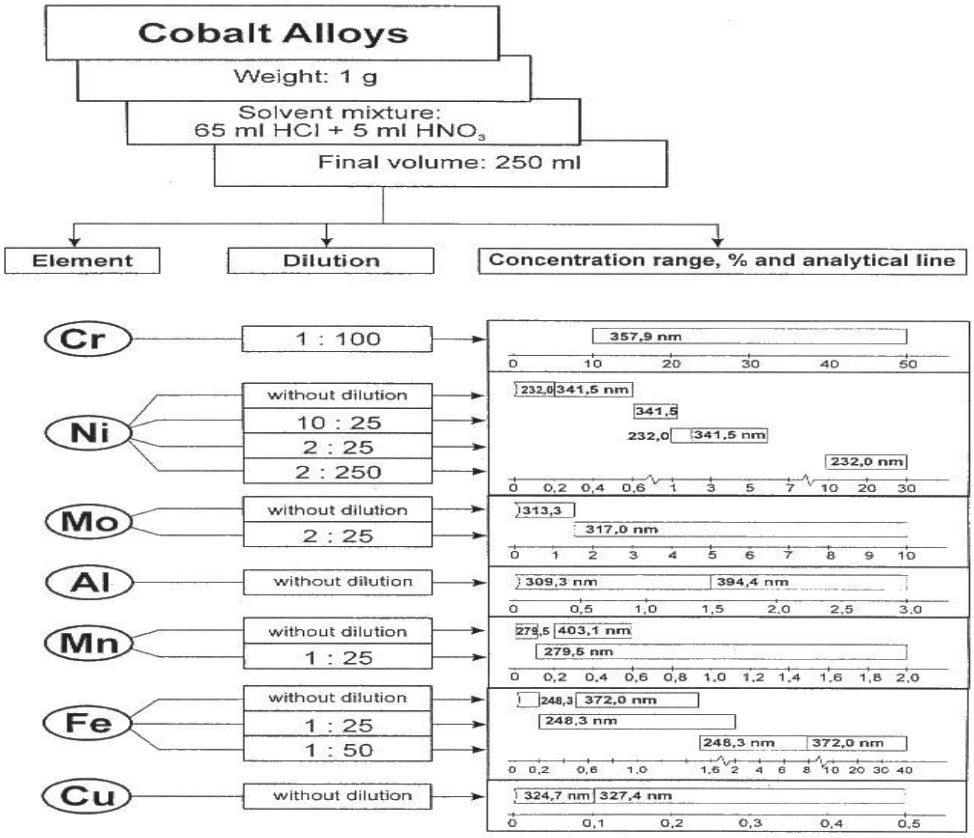

FIGURE 1. Analytical diagram for analysis of cobalt alloys by AAS method

The following chemical reagents, analytically pure, have been used to perform determinations: hydrochloric acid (1.19), nitric acid (V) (1.4) and cobalt chloride (II) – $CoCl_2 \cdot 6H_2O$. The stock standard solutions of 50 mg Co/ml were prepared by dissolving 200 g of analytical grade $CoCl_2 \cdot 6H_2O$ in distilled water and dilute to 1 liter. The obtained solutions were stored in tightly closed polythene containers.

3. SAMPLE PREPARATION

The weighed amount of 1 g of cobalt alloy was dissolved in 65 ml of HCl (1:1), if necessary by heating slowly on a hot plate until to the end of reaction. Then 5 ml of conc. HNO_3 were added and the content of beaker was carefully evaporated to near dryness. The residue was allowed to cool, 15 ml HCl (1:1) and 30 ml H_2O were added. The solution was heated to boiling to dissolve the salts, cooled and the solution diluted with distilled water to the mark of 250 ml polypropylene flask. The obtained solution was poured to a polythene bottle with a tight closure.

4. STANDARD PREPARATION

Taking into account inter-element influences in the case of a cobalt matrix (3,4,7,9,10,13) to determine the chemical composition of cobalt alloys the method of a single specific standard has been applied and presented in Table 2. Appropriate weighed amounts of specific (initial) standard (S_1-0,8 g, S_2-0,85 g, S_3-0,9 g, S_4-0,95 g and S-1,0 g) were selected in such a way that the sought concentration was limited by known contents of this element in standard solutions. The specific standard is "qualitatively" selected for the investigated sample. It is also significant that the upper and lower values of individual elements concentrations occur in the linear range of standard curves. To maintain the same conditions during preparing standard solutions the sequence of individual operations shall be the same as during preparing sample solutions. After dissolution of salts add to each standard solutions S_1, S_2, S_3 and S_4 respectively 4, 3, 2 and 1 ml the stock standard solution of cobalt (50 mg Co/ml) and diluted with distilled water to the mark of 250 ml polypropylene flask. A blank sample consisted of reagents used in analysis.

TABLE 2. Selection of specific standard for analysis of cobalt-base alloys

Elements		Co	Cr	Ni	Mo	Al	Mn	Fe	Cu
Chemical composition of specific standard, %		(77.5)	16.40	1.60	1.86	1.64	1.55	0.85	0.25
Weighed amounts, g	S_1 – 0.8000	(62.0)	13.12	1.28	1.49	1.31	0.68	0.68	0.20
	S_2 – 0,8500	(65.9)	13.94	1.36	1.58	1.39	0.72	0.72	0.21
	S_3 – 0,9000	(69.8)	14.76	1.44	1.67	1.48	0.77	0.77	0.23
	S_4 – 0.9500	(73.6)	15.58	1.52	1.77	1.56	0.81	0.81	0.24
	S – 1.0000	(77.5)	16.40	1.60	1.86	1.64	0.85	0.85	0.25
Measuring range, %			13.12 16.40	1.28 1.60	1.49 1.86	1.28 1.60	0.68 0.85	0.68 0.85	0.20 0.25
Amount of metallic Co added to standards, g		Reference to S standard – weighed amount Co content in solution, mg Co/ml							
		S_1 0.2000				3.28			
		S_2 0.1500				3.24			
		S_3 0.1000				3.19			
		S_4 0.0500				3.15			
		S 0.0000				3.10			

5. RESULTS AND DISCUSSION

Experimental values obtained for some cobalt alloys are given in Table 3. The accuracy of the results may be as the obtained results, a part of which is presented in Table 3, fully confirm a right strategy of analytical procedure and usefulness of the briefly discussed calibration method using one specific standard for chemical analysis of cobalt alloys. The obtained results of investigations were also verified statistically, comparing two mean values using Student's t-test (1). All the obtained investigations results have been positively verified, i.e. differences in individual elements determined according to a variant of one specific standard did not differ significantly. The precision of the determinations of the given elements in cobalt alloys (analysis of different alloys) was as follows: Cr 1.08 – 1.38 %, Ni 0.95 – 1.25 %, Mo 1.09 – 1.31 %, Al 1.09 – 1.22 %, Mn 0.81 – 1.08 %, Fe 1.79 – 2.65 % and Cu 1.36 – 1.66 %.

TABLE 3. Results of chemical analysis of cobalt alloys by the AAS method

Element	Chemical, %	Found, %	Standard Deviation	Coefficient of variation, %
Cr	13.28 16.10	13.1 16.0	0.181 0.172	1.38 1.08
Ni	1.38 1.54	1.37 1.52	0.013 0.019	0.95 1.25
Mo	1.62 1.85	1.60 1.83	0.021 0.020	1.31 1.09
Al	1.41 1.56	1.39 1.58	0.017 0.020	1.22 1.09
Mn	1.37 1.48	1.39 1.49	0.015 0.012	1.08 0.81
Fe	0.70 0.79	0.68 0.78	0.018 0.014	2.65 1.79
Cu	0.22 0.25	0.22 0.24	0.003 0.004	1.36 1.66

This method of calibration is very useful in physical metallurgy investigations performed, e.g. to optimize melting parameters or even more frequently to variants of thermal treatment of the given Co-alloy. When planning such investigations based on specific data on experiment planning it is worth to take pains of performing a preparation of cobalt alloy selected as a specific standard to gain more in term of time and labour intensity during the determination of chemical composition of series of cobalt alloys thus omitting the preparation of synthetic standard solutions.

REFERENCES

1. EKSCHLAGER K., Errors in chemical analysis, PWN, Warszawa 1974 (in Polish)
2. HERNAS A. and MACIEJNY A., High-temperature alloys of metals, Metallurgical Committee of the Polish Academy of Sciences, Zakład Narodowy Imienia Ossolińskich Wrocław, 1989 (in Polish)
3. NESTOROVA E., MINCHEVA V., Metalurgiya (Sofia) 1986, 43, p. 24
4. SCHINKEL H., Störungen der Flammen-ES und -AAS Ursachen Auswirkungen Gegenmassnahmen, Ottweiler Druckerei und Verlag 1997
5. SIMS C.T., HAGEL W.C., THE SUPERALLOYS, J. WILEY Interscience Publication, New York 1972
6. VAN LOON J.C., Analytical Atomic Absorption Spectroscopy. Selected Methods, Academic Press 1980, New York London Toronto Sydney San Francisco
7. VOGLIOTTI F.L., At. Absorption Newslett., 1970, 9, p. 123
8. WELCHER G.G., KRIEGE O.H., At. Absorption Newslett. 1970, 9, p. 61
9. WELZ B., Atom-Absorptions-Spektrometrie, Verlag Chemie, Weinheim Deerfield Beach, Florida, Basel 1999
10. WYCIŚLIK A., Chem. Anal. (Warsaw) 1999, 44 p. 755
11. WYCIŚLIK A., Conf. Materials Analytical Metrology II – Methods of calibration in analytical chemistry, Ustroń 1993, p.20 (in Polish)
12. WYCIŚLIK A., Inżynieria Materiałowa (Poland) 1984, 5, p. 191
13. WYCIŚLIK A., Mikrochim. Acta 1990, II, p. 287