VOLUMETRIC DETERMINATION OF COBALT IN CoSmFe ALLOYS USING A SILVER ION SELECTIVE ELECTRODE IN AQUEOUS DIMETHYLFORMAMIDE AND IN WATER

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A procedure is suggested for direct volumetric determination of cobalt with a sodium diethyl-dithiocarbaminate titrant solution in the medium of 80% dimethylformamide, using indication with a silver ion selective electrode. The procedure was applied to the cobalt determination in Co–Sm–Fe alloys. The method was adapted for the determination of cobalt in aqueous solutions by back titration of excess sodium diethyldithiocarbaminate with a silver nitrate titrant solution or with generated Ag(I), using the same indication or biamperometric indication.

The present work follows up our previous study[1,2] dealing with the volumetric and photometric determination of lanthanoids in alloys of heavy metals. This work is concerned with the problem of volumetric determination of cobalt in Co–Sm–Fe alloys, which are materials of interest for the manufacturing of novel permanent magnets[3]. Direct and indirect titrimetric methods are suggested employing sodium diethyldithiocarbaminate as the reagent and a silver ion selective electrode for the indication.

Ion selective electrodes (ISE) are increasingly employed for the indication of titration end points in direct titration procedures leading to products constituting a part of the electrode material[4–6] or in back titration methods, where the metal determined is not a part of the electrode[6–9]. In most procedures of metal determination where ion selective electrodes are used, however, chelatons are applied as the titrants[10–13].

EXPERIMENTAL

Apparatus

For the electrochemical indication of the titration end point of the direct and back titrations, an Ag-ISE Crytur 47–17 (Monokrystaly, Turnov) was employed in conjunction with a saturated calomel electrode (s.c.e.) equipped with a graphite tip (Druopta, Prague). The electrodes were interconnected *via* a salt bridge of 10% KNO_3. The cell voltage was measured by means of a pH--meter PHM 22r (Radiometer, Copenhagen) or a technical compensator L 121 (Metra, Blansko).

The Ag(I) generation, coulometric titrations, and biamperometric indication were accomplished on a Coulometer 404 (Radelkis, Budapest).

Chemicals and Solutions

The cobalt standard solutions were prepared from a 99·999% Co standard (Mathey–Johnson, England). The chemicals and solvents used were reagent grade purity (Lachema, Brno).

Working Procedure

The Co–Sm–Fe alloys (500 mg) or Co (350 mg) were dissolved in a minimal volume (2 ml) of nitric acid (1 : 1). After dissolution and removing of nitrogen oxides the solution was diluted with water and brought to the volume of 200 ml with water or with dimethylformamide (DMF) so that the DMF concentration was 80% (v/v). For the direct titrations in 80% DMF, an aliquot (1 — 10 ml) was diluted with 80% DMF to such a degree that the concentration of cobalt was not lower than 5 mg/10 ml. As the titrant solution served $2 . 10^{-2}$ or $4 . 10^{-2}$ M sodium diethyl-dithiocarbaminate (NaDDC) in 80% DMF.

For the back titrations in aqueous medium, an aliquot was neutralized with 2M-NH$_4$OH and adjusted to pH 7—8·5. The concentration applied was 2—20 mg Co/10 ml. Excess $4 . 10^{-2}$ to 10^{-1} M-NaDDC was added and titrated with $4 . 10^{-4}$ M-AgNO$_3$ or with generated Ag(I).

For the coulometric titrations in aqueous solutions, the generation was performed employing currents 10 mA, the voltage applied to the pair of the indication platinum electrodes for the biam-perometric indication was about 0·9 V.

The content of iron in the alloys analyzed was below 1%, thus the Fe(III) had not to be removed for routine determinations. For accurate determinations, Fe(III) was removed by extraction with 1% solution of acetylacetone in chloroform[14]. After repeated extraction and phase separa-tion, the chloroform residue was removed by extraction with benzene.

The titres of the titrant solutions used were determined by employing the cobalt reference standard in the same working conditions as applied to the subsequent determinations. The end points were read off the first order derivative curves. The evaluation of the results obtained from 3—4 sets of measurements comprised the calculation of the standard deviation estimate s and the relative error of the average e.

RESULTS AND DISCUSSION

Ion selective electrodes for the determination of cobalt are not commonly available; therefore we sought for some other electrodes that would respond to the concentra-tion of Co(II). Cobalt cations give rise to a high response of copper and silver ion selective electrodes, the response being enhanced in some organic solvents as compared with aqueous medium, which offers a basis for increasing the sensitivity of the method. However, in nonaqueous organic solvents the application is con-strained by the dissolution of the binders employed for the manufacturing of the electrodes. This limiting factor led us to use 80% (v/v) dimethylformamide, in which no depreciation of the electrodes was observed even after one year's service. The sensitivity of the Ag-ISE to the Co(II) concentration was better as compared with the Cu-ISE; the former was therefore employed for the volumetric determinations. We developed a procedure of direct titrimetric determination of cobalt in 80% DMF

with a solution of NaDDC, which in this medium forms stable soluble complexes $Co(DDC)_2$, whose stability causes the titration end point to manifest itself by a high and steep potential jump $(400 - 500$ mV for $3 - 10$ mg Co$)$.

There are two principal advantages of NaDDC over other chelating agents such as Chelaton III or IV. One is the high stability of the $Co(DDC)_2$ complex in comparison with the Co-chelaton complexes[14-16], the other is the higher selectivity of NaDDC, which in the conditions suggested does not afford products with Sm, as against the chelatons reacting with lanthanoids[16]. The potential jumps pertaining to the equivalence points of Co and Sm in titrations with chelatons are indistinct $(50 - 80$ mV); during the determinations with NaDDC there appears a single potential jump, which is very pronounced and corresponds to the equivalence point of Co. The results of the direct volumetric determinations of cobalt in 80% DMF are given in Table I.

TABLE I

Results of Determination of Cobalt by Direct Titration with $4 . 10^{-2} - 2 . 10^{-2}$M Sodium Diethyldithiocarbaminate Titrant Solution in 80% Dimethylformamide, Indication Ag-ISE vs S.C.E.

Prepared mg	Found (average) mg	s^a	e^b %	Prepared mg	Found (average) mg	s^a	e^b %
Co standard^c				Co–Sm–Fe alloy (30·05% Sm)^d			
1·02	1·07	0·06	+4·9	3·50	3·31	0·14	− 5·4
1·70	1·76	0·05	+3·5	4·55	4·62	0·07	+ 2·4
3·40	3·45	0·06	+1·4	7·00	7·20	0·15	+ 2·8
5·10	5·00	0·01	−2·0	14·00	15·00	0·61	+ 7·1
6·80	7·04	0·27	+3·5				
10·20	9·93	0·27	−2·6	Co–Sm–Fe alloy (34·04% Sm)^d			
13·60	13·24	0·27	−2·6				
20·40	20·26	0·30	−6·8	3·30	3·45	0·17	+ 4·5
				6·60	6·90	0·22	+ 4·5
Co standard + 44% Sm^d				13·20	12·93	0·26	− 2·0
1·70	1·77	0·05	+4·1				
3·40	3·36	0·06	−1·2				
5·10	5·20	0·07	+2·0				
10·20	9·90	0·21	−2·9				
13·60	14·10	0·36	+3·7				

^{a} Standard deviation estimate; ^{b} relative error of the average; ^{c} four parallel determinations; ^{d} three parallel determinations.

For the direct volumetric determination of Co with NaDDC in dimethylformamide it is important that the $Co(DDC)_2$ complex formed should be quantitatively dissolved in the solution. This requires the suggested ratio of the component determined to the volume of the solvent mixture to be adhered to; when the dilution is insufficient, the green precipitate of the complex separates out of the solution, which is associated with a break on the titration curve. With regard to this constraint it is expedient to apply quantities of 2—10 mg Co for the determinations, to avoid consumption of large volumes of the titrant solution.

During attempted direct volumetric determination of cobalt in aqueous medium, a lower response was obtained with the copper as well as the silver ion selective electrodes. Due to the lowered steepness, the titration curves were not suitable for quantitative evaluation. For this reason we chose a back titration method for aqueous solutions such that use could be made of the high sensitivity of the Ag-ISE to the concentration of Ag(I): excess NaDDC was titrated with silver nitrate titrant solu-

TABLE II

Results of Cobalt Determination by Back Titration of Excess Sodium Diethyldithiocarbaminate with $4 \cdot 10^{-2}$M-$AgNO_3$ or the Generated Ag(I) in Aqueous Solutions

Prepared mg	Found (average) mg	s^a	e^b %	Prepared mg	Found (average) mg	s^a	e^b %
	Co standard				Co–Sm–Fe alloy (30·05% Sm)		
1·02	1·05	0·07	−2·9	3·50	3·40^c	0·09	− 2·9
3·40	3·42	0·04	+0·6	7·00	6·80^c	0·12	− 2·9
6·80	6·60	0·06	−2·9	10·50	10·80^c	0·12	+ 2·9
7·00	7·07	0·08	+1·0				
10·20	10·30	0·25	+1·0	3·50	3·60^d	0·09	+ 2·9
13·60	13·47	0·01	−1·0	7·00	8·00^d	0·27	+14·3
27·20	27·40	0·19	+0·7	14·00	13·50^d	0·15	− 3·6
	Co standard + 44% Sm						
3·40	3·42	0·04	+0·6	3·50	4·10^e	0·12	+17·1
6·80	6·70	0·04	−1·5	7·00	8·20^e	0·30	+17·1
13·60	13·73	0·06	+0·9	14·00	13·00^e	0·27	− 7·1

^{a} Standard deviation estimate; ^{b} relative error of the average; ^{c} back titration with 0·04M-$AgNO_3$, indication: Ag-ISE vs S.C.E.; ^{d} coulometric titration, indication: Ag-ISE vs S.C.E.; ^{e} coulometric titration, indication: biamperometric; $n = 3$.

tion or with generated Ag(I). The results of the back titrations of the cobalt standard, both without and with an addition of samarium, as well as those of the cobalt de-determination in the Co–Sm–Fe alloys analyzed are given in Table II.

In aqueous solutions it is important that the free nitric acid, employed for the dissolution of the alloys, be neutralized. The pH of the solution to be titrated is adjusted to $7-8.5$ with 2M-NH$_4$OH. In aqueous solutions the product Co(DDC)$_2$ formed is highly insoluble, $K_s < 10^{-22}$, the effect of dilution is therefore not very important. The cobalt content may lie in the range $2-20$ mg/ml, which enables titration of greater cobalt quantities, the volume of $10-15$ ml being maintained. For the coulometric titrations, in addition to the common biamperometric indication we employed also indication with the Ag-ISE vs S.C.E, where a small excess of Ag(I) above the end point gives rise to a high potential change (about 0.6 V).

The results of the direct and indirect volumetric determinations of the standard solutions as well as of the alloys show that by the procedure suggested it is possible to determine $1-20$ mg Co with $4 . 10^{-2}-2 . 10^{-2}$M-NaDDC, no buffers or masking agents and no preliminary separation of cobalt from samarium being needed. The direct volumetric determination of cobalt can be conducted in 80% (v/v) dimethylformamide and is suitable for contents of $2-10$ mg Co. In aqueous solutions, the indirect determination based on the titration of excess sodium diethyldithiocarbaminate with $4 . 10^{-4}$M-AgNO$_3$ is suitable; the cobalt contents of $3-20$ mg/10 ml are appropriate. If the above dilutions are applied, the standard deviation estimate does not exceed 0.2.

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