

TITRIMETRIC DETERMINATION OF COBALT, NICKEL AND LANTHANOIDS IN ALLOYS FOR NOVEL PERMANENT MAGNETS USING ION SELECTIVE ELECTRODES

Dagmar KALAVSKÁ^a, Adam KOŠTURIÁK^b and Svetozár KALAVSKÝ^c

^a Department of Analytical Chemistry,
Comenius University, 816 50 Bratislava,

^b Department of Experimental Physics,
Šafárik University, 415 40 Košice and

^c Department of General Physics,
Comenius University, 816 50 Bratislava

Received October 23rd, 1979

A procedure of chelatometric determination of cobalt, nickel, and lanthanoids based on back titration with Cu(II) ions using copper ion selective electrode has been developed and applied to alloys for novel type permanent magnets. In addition, a method has been worked out for direct titrimetric determination of lanthanoids with solution of fluoride ions in 75% ethanol using fluoride ion selective electrode.

In the development of intermetallic alloys for novel types of permanent magnets there is a need for a method for determination of the constituents of cobalt-lanthanoid and nickel-lanthanoid type alloys. The present study follows up the work¹, in which a procedure has been worked out for volumetric determination of cobalt in CoSmFe alloys, and the work², concerned with chelatometric determination of lanthanoids using metalochromic indicators. In the present work, the problem of a complex volumetric determination of the components in the above type alloys is tackled.

EXPERIMENTAL

Apparatus

A Crytur 07-17 lanthanum fluoride ion selective electrode (F-ISE) (Monokrystaly, Turnov) was used for electrochemical indication of the end point in direct titrimetric determination of lanthanoids with sodium fluoride, and a Crytur 29-17 copper ion selective electrode (Cu-ISE) of the same manufacturer was employed for determination of lanthanoids, nickel, and cobalt by retitration of excess Chelaton with copper nitrate. The electromotive force of the cell comprising the ISE and a saturated calomel electrode interconnected by a 10% KNO₃ salt bridge was measured on an OP-264 digital pH/mV-meter (Radelkis, Budapest). The pH values were measured on a PHM 22r pH-meter equipped with a G202B—K100 electrode pair (Radiometer, Copenhagen).

Chemicals and Solutions

The standard solutions of Co and Ni were prepared from the 99.999% metals (Mathey-Johnson, England), the standard solutions of lanthanoids were prepared from the respective metals or oxides (Soyuzkhimexport, Moscow). The other chemicals used were reagent grade purity (Lachema, Brno). The NaF titrant solution was prepared from a known amount of the dried chemical, the $\text{Cu}(\text{NO}_3)_2$ titrant solution was prepared from electrolytic copper, and the solutions of Chelaton 3 and Chelaton 4 were made up by converting the respective acids (ethylene diaminetetraacetic and diaminocyclohexanetetraacetic acids) to the diammonium salts by adding the stoichiometric quantity of ammonia and adjusting the pH to 6.5–7.0. All the solvents were redistilled prior to use.

Working Procedure

The alloys, metals or oxides (200–500 mg) were dissolved in a minimal volume of HNO_3 (1 : 1), and after removing nitrogen oxides, diluted to 100 ml. For the determination of lanthanoids in standard solutions and in the solutions of alloys, 2–7 mg portions were used, a minimal

TABLE I

Determination of Lanthanoids by Direct Titration with NaF and by Retitration of Excess Chelaton 3 or Chelaton 4 with $\text{Cu}(\text{NO}_3)_2$

Titration with $2 \cdot 10^{-2} \text{ mol l}^{-1}$ NaF in 75% (v/v) ethanol: F-ISE vs S.C.E., $\Delta E/\Delta V \approx 270 \text{ mV/ml}$; retitration of Chelaton 3 or 4 ($2 \cdot 10^{-2} \text{ mol l}^{-1}$) with $2 \cdot 10^{-2} \text{ mol l}^{-1}$ $\text{Cu}(\text{NO}_3)_2$: Cu-ISE vs s.c.e., $\Delta E/\Delta V \approx 160 \text{ mV/ml}$.

Element	Prepared mg	Titration with NaF			Retitration of Chelaton 3			Retitration of Chelaton 4		
		found ^a mg	s_r^b %	e^c %	found mg	s_r %	e %	found mg	s_r %	J %
La	1.390	1.380	1.44	-0.72	1.375	2.91	-1.08	—	—	—
	4.167	4.113	1.44	-1.30	4.200	1.20	0.79	4.150	0.96	-0.41
Ce	1.401	1.388	2.16	-0.93	1.398	1.43	-0.21	1.475	4.07	5.28
	4.203	4.252	1.41	1.17	—	—	—	4.410	1.14	4.93
Pr	1.409	1.490	4.70	5.75	—	—	—	—	—	—
	4.227	4.380	1.83	3.62	4.350	2.53	2.91	4.120	3.88	-2.53
	8.454	8.550	0.94	1.14	—	—	—	8.570	1.17	1.37
Sm	1.642	1.600	4.38	-2.56	1.630	6.75	-0.73	1.651	4.85	0.55
	4.925	4.942	1.01	0.35	4.850	2.89	-1.52	5.000	3.20	-1.52
Gd	1.900	1.890	4.76	-0.53	—	—	—	2.000	4.00	5.26
	5.700	5.65	1.42	-0.88	5.655	1.77	-0.79	—	—	—

^a Average of four determinations; ^b relative standard deviation of the average; ^c relative error of the average.

volume (0.5—1.0 ml) of 0.5M urotropine or ammoniacal buffer was added for pH adjustment to pH 6—7, and the solution was diluted with ethanol so that its content in the total volume of 6—8 ml was 75% (v/v). A solution of $2 \cdot 10^{-2} \text{ mol l}^{-1}$ NaF in 75% (v/v) ethanol served as the titrant and an F-ISE vs s.c.e. cell as the indicating system.

For the chelatometric determination of lanthanoids as well as of cobalt and nickel, the same batches were used in aqueous solutions pH \approx 7.0 (urotropine, NH_3); the excess complexone

TABLE II

Determination of Lanthanoids and Heavy Metals in Standard Mixtures by Direct Titration with NaF and by Retitration of Excess Chelaton 3 or Chelaton 4 with $\text{Cu}(\text{NO}_3)_2$

Titration with $2 \cdot 10^{-2} \text{ mol l}^{-1}$ NaF in 75% (v/v) ethanol: F-ISE vs s.c.e., $\Delta E/\Delta V \approx 200 \text{ mV/ml}$; retitration of $2 \cdot 10^{-2} \text{ mol l}^{-1}$ Chelaton 3 or 4 with $2 \cdot 10^{-2} \text{ mol l}^{-1}$ $\text{Cu}(\text{NO}_3)_2$: Cu-ISE vs s.c.e., $\Delta E/\Delta V \approx 160 \text{ mV/ml}$.

Element	Prepared mg	Titration with NaF			Retitration of Chelaton 3			Retitration of Chelaton 4		
		found ^a	s_r	e	found	s_r	e	found	s_r	e
		mg	%	%	mg	%	%	mg	%	%
La-Co										
La	2.778	2.795	2.15	0.61	2.690	4.09	-3.17	2.808	3.21	1.08
Cow	5.890	—	—	—	—	—	—	5.962	1.85	1.22
La-Ni										
La	2.778	2.885	2.08	3.85	—	—	—	—	—	—
Ni	5.870	—	—	—	6.010	4.99	2.39	5.755	2.95	-1.96
Sm-Co										
Sm	3.001	3.000	1.67	-0.03	—	—	—	3.100	3.87	3.30
Cow	6.350	—	—	—	6.500	3.69	2.36	6.210	2.42	-2.20
Sm-Ni										
Sm	3.001	2.890	3.11	-3.70	2.980	3.36	-0.70	2.902	5.51	-3.30
Ni	5.870	—w	—	—w	5.895	3.17	1.96	6.004	3.33	2.28
Gd-Ni										
Gd	1.900	2.007	3.49	5.63	—	—	—	1.987	4.53	4.58
Ni	5.870	—	—	—	—	—	—	5.965	2.35	1.62

^a Average of four determinations.

(Chelaton 3 or 4) was titrated with solution of $2 \cdot 10^{-2} \text{ mol l}^{-1} \text{ Cu}(\text{NO}_3)_2$ using Cu-ISE vs S.C.E. cell. When Co and Ni were determined, an approximately 60-fold excess of NH_4F was added to the lanthanoid, the mixture was heated for 5 min, and after cooling down, titrated with solution of Cu(II).

RESULTS

As pointed out previously¹, Ag-ISE and Cu-ISE respond appreciably to Co or Ni ions, which offers a means for their direct chelatometric determination. In direct titrations of a heavy metal and lanthanoid in medium of a neutral or weakly basic buffer, two potential jumps are obtained, but they are not very pronounced and their $\Delta E/\Delta V$ values are highly dependent on the pH, solution composition, and heavy metal-to-lanthanoid concentration ratio. Applying different working conditions we were able to demonstrate that this way of determination cannot be looked upon as universal for different concentration ratios of the two cations concerned, as the potential changes in some cases are associated with the appearance of a turbidity on account of formation of lower complexes. For this reason we pursued other ways of determination: chelatometric back titrations³⁻⁶ of Ni and Co; chelatometric titrations^{7,8} of lanthanoids; and titrimetric determination of lanthanoids with

TABLE III

Determination of Lanthanoids, Cobalt and Nickel in Alloys for Permanent Magnets
Concentration of the titrant solutions $2 \cdot 10^{-2} \text{ mol l}^{-1}$.

Alloy	Element	Content		Prepared mg	Titration with NaF		Retitration of Chelaton 3		Retitration of Chelaton 4	
		assumed ^a %	found ^b %		found ^c mg	s_r %	found mg	s_r %	found mg	s_r %
SmCo ₅	Sm	33.785	34.04	3.94	4.04	3.42	3.82	4.18	3.63	4.13
	Co	—	—	7.63	—	—	7.18	4.18	7.56	3.04
PrCo ₅	Pr	32.35	—	1.26	1.24	6.45	—	—	1.11	9.91
	Co	—	—	2.64	—	—	—	—	2.58	4.65
GdNi ₂	Gd	57.25	57.48	2.74	2.76	2.90	2.86	3.49	2.63	3.80
	Ni	—	—	2.00	—	—	1.90	5.79	2.06	4.85
Gd ₃ Ni	Gd	88.93	88.98	7.83	7.83	0.77	7.67	1.17	7.92	3.41
	Ni	—	—	0.97	—	—	1.04	10.58	0.80	13.75
GdNi ₅	Gd	34.88	35.79	1.07	1.11	5.41	—	—	—	—
	Ni	—	—	1.91	—	—	2.00	4.50	1.88	4.79

^a Based on the weight ratio during the melting; ^b refs^{1,2}; ^c average of four determinations.

fluoride titrant solution^{9,10}. In our experiments, solutions containing the metals in quantities of the order of magnitude 10^{-3} g were titrated with titrant solutions of the concentration 0.02 mol l^{-1} . In the chelatometric titration the pH had to be held¹¹ at a value ≥ 7.0 . Using milligram amounts of the metals, the potential change in the end point range was $\Delta E/\Delta V \approx 200 \text{ mV/ml}$ for the standard solutions and $\approx 170 \text{ mV/ml}$ for the solutions of the alloys. The procedure was tested with standard solutions of lanthanoids and with solutions of lanthanoid-heavy metal mixtures (Tables I and II). No differences were found in the course and results of determination with Chelaton 3 and Chelaton 4, although the latter gives rise to more stable chelates.

The results of determination of lanthanoids with NaF in 75% (v/v) ethanol in the standard solutions and their mixtures are also given in Tables I and II. In the case of the lanthanoid standards, the $\Delta E/\Delta V$ value in the end point range is 270 mV/ml , in the mixtures with a heavy metal it is approximately 210 mV/ml . The effect of Co and Ni with regard to the possible formation of their fluoro complexes was examined by masking them with phenanthroline and 1-nitroso-2-naphthol. The results in the presence and in the absence of the masking agents were identical, which indicates that such Co or Ni fluoro complexes, which could affect the results of determination, are not formed. The possibility of determination of lanthanoids by retitration of excess NaF with $\text{Th}(\text{NO}_3)_4$ was also examined. In this case the pH does not affect the determination – the titration could be accomplished at pH 2–6 using F-ISE, $\Delta E/\Delta F \approx 300 \text{ mV}$ – but on the whole the procedure does not offer advantages over the direct titration method. The results of determination of Co, Ni, and lanthanoids are summarized in Table III and compared with those arrived at using the procedures described in^{1,2}.

In the procedures applied using Cu-ISE and F-ISE, the parameters characterizing the precision (s_r) and accuracy (e) did not exceed 5%.

REFERENCES

1. Košturiak A., Kalavská D.: This Journal **44**, 1742 (1979).
2. Košturiak A., Kalavská D.: Acta Fac. Rerum Natur. Univ. Comenianae, in press.
3. Van der Meer J. M., den Boef G., Van der Linden W. E.: Anal. Chim. Acta **76**, 261 (1975).
4. Baumann E. W., Wallace R. M.: Anal. Chem. **41**, 2072 (1969).
5. Van der Meer J. M., den Boef G., Van der Linden W. E.: Anal. Chim. Acta **79**, 27 (1975).
6. Ross J. W., Frant M. S.: Anal. Chem. **41**, 1900 (1970).
7. Šůcha L., Suchánek M.: Anal. Lett. **3**, 613 (1970).
8. Cammann K.: *Das Arbeiten mit Ionselektiven Elektroden*, p. 165. Springer, Berlin, Heidelberg, New York 1977.
9. Lingane J. J.: Anal. Chem. **39**, 881 (1967); **49**, 935 (1968).
10. Šůcha L., Suchánek M., Urner Z., Sluka V.: Sb. Vys. Šk. Chemicko-Technol. Praha **H 12**, 213 (1977).
11. Tikhonov V. N.: Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol. **21**, 144 (1978).

Translated by P. Adámek.