Extractive-photometric determination of microquantities of cerium in some metallic materials

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The described colour reaction of Ce(III) with arzenazo III in glycine buffer solutions of pH = 2.5—pH = 3.1 depending on composition of the analyzed material is used to sensitive photometric determination of Ce(III) even in multicomponent systems such as crude iron and different kinds of steel. This reaction is usually combined with extraction, screening or electrolytic separation of excess interfering ions as well as with extraction of the determined cerium in the form of the Ce(III)—phenylacetic acid complex from urotropine buffer solution (pH = 8—pH = 9) into n-butyl alcohol. These procedures are followed by reextraction and analytical determination.

The obtained results have been evaluated by different mathematical-statistical methods and confronted with the relations which allow simultaneous estimation of precision and accuracy of the results of analyses and are convenient for estimation of the width of tolerance corridor depending on concentration of the analyzed sample even if the measurements are not many times repeated.

Раннее описанная цветная реакция Ce(III) с арсеназо III в глициновых буферных растворах с pH = 2,5—pH = 3,1 в зависимости от состава анализируемого материала используется в комбинации экстракцией, нивелированием и электролитическим отделением больших избытков мешающих ионов, или же с экстракцией определяемого церия в форме комплекса Ce(III)—фенилуксусная кислота из уротропинового буферного раствора с pH = 8—pH = 9 в н-бутиловый спирт и последующим его определением после ре-экстракции, к его чувствительному фотометрическому определению в многокомпонентных системах, какими являются сырое литье и стали.

Полученные результаты обрабатываются различными, обычно применяемыми математическо-статистическими методами и затем сопоставляются с аналогичными найденными зависимостями, позволяющими одновременно оценивать точность и достоверность методов анализа, которые можно применить и при не очень часто повторяемых измерениях для оценки их коридоров допустимых отклонений в зависимости от концентрации анализируемого образца.

This contribution starts from paper [1] which was concerned with reaction conditions of spectrophotometric determination of microquantities of lanthanoides by means of arzenazo III (A III). These lanthanoides were present in simple metal systems in which the influence of trace amounts of interfering elements could be screened with sulfosalicylic acid and α,α'-bipyridyl after eliminating the influence of main components. However, this method could not be satisfactorily applied to materials such as crude iron and espacially different kinds of steel which have complicated chemical composition and are important from the view-point of technology and technique. Therefore further stage in optimization of the determination necessitated to find out some procedures which could enable us to eliminate the influence of higher content of interfering elements which might be present in crude iron and steel. For this purpose, we used new procedures based on extractive separation of cerium, especially in the form of the Ce(III)—phenylacetic acid complex [2].

Experimental

The starting, *i.e.* basic conditions of experiment are described in detail in paper [1] where the analytical procedures for direct photometric determination of Ce(III) with A III are presented (Procedure A).

Procedure B

The separation of cerium in the form of the complex containing phenylacetic acid may be performed in the samples from which the high content of interfering elements was eliminated by the procedures presented in paper [1]. We may proceed as follows: The urotropine buffer solution is so added into the sample which does not contain more than 100 μg Ce(III) that the pH value is 8.5 ± 0.5. Then 3 cm³ of 5 % phenylacetic acid dissolved in ethyl alcohol are added and after 2 min, the extraction with n-butyl alcohol follows. Then the complex of Ce(III) containing phenylacetic acid is reextracted from the organic phase into HCl (HNO₃) ($c = 0.1$ mol dm⁻³) or still better into the glycine buffer solution so that its pH value is 2.5—3.1. Afterwards, the sample is treated according to procedure A.

Procedure C

The interfering elements which cannot be removed by their extraction with diethyl ether or n-amyl acetate and their influence is not to be screened by α,α'-bipyridyl and sulfosalicylic acid may be separated by extraction with cupferron into n-butyl alcohol [2] in this way: A 1 % solution of cupferron is gradually added into the analyzed sample the pH value of which varies in the range pH = 1—pH = 2 and the formed precipitates are extracted with n-butyl alcohol. Cupferron is added as long as the precipitates arise.

We may also so proceed that we first remove the interfering elements with cupferron and extract cerium with phenylacetic acid.

The calculation of statistical parameters of the regression line was carried out with a digital computer Minsk 21 (USSR) according to current programs. The estimates of standard deviations and errors of measurements were performed according to the relations given in [3].

The absolute and relative value of standard deviation of the arithmetic mean $s(\bar{x})$ and $s_r(\bar{x})$ was calculated by means of the following formulae

$$s(\bar{x}) = \sqrt{\frac{\Sigma \Delta^2}{n(n-1)}} \qquad s_r(\bar{x}) = \frac{100\, s(\bar{x})}{m}$$

where $\Sigma \Delta^2$ is the sum of squared deviations of individual values of measurements from the arithmetic mean, n is the number of measurements, and m denotes the mass of the analyzed sample.

The absolute and relative value of standard deviation of individual measurement was calculated from the relationships

$$s(x) = \sqrt{\frac{\Sigma \Delta^2}{n-1}} \qquad s_r(x) = \frac{100\, s(x)}{m}$$

or

$$s(R) = k_n R \qquad s_r(R) = \frac{100\, s(R)}{m}$$

where R is the span and k_n is the statistical coefficient derived on the basis of mathematical-statistical considerations concerning small ensembles of results. The values of this coefficient are tabulated.

The relative error of the arithmetic mean was calculated from the following formula

$$d_r(\bar{x}) = \frac{100(\bar{x} - \mu)}{\mu}$$

where $\bar{x}$ is the arithmetic mean and μ is the real value.

The estimates of the absolute and relative values of standard deviations s_v and $s_{r,v}$ as well as of relative errors $d_{r,v}$ were based on the relationships presented in papers [4, 5]

$$s_v = \sqrt{\frac{\Sigma \Delta^2 \bar{n} u k_{\bar{n}} m}{n(\bar{n}-1)(u-1)\, by_{v\,\max}}} \qquad s_{r,v} = \frac{100\, s_v}{m}$$

$$d_{r,v} = \frac{100}{m} \sqrt{\frac{\Sigma \Delta^2 u m}{n(u-1)\, by_{v\,\max}}}$$

where $\bar{n}$ is the average number of determinations of the total number of determinations n which falls on a certain individual concentration. It holds

$\bar{n} = n/u$, where u is the number of individual concentrations (knots) in the investigated concentration interval. The symbols b, $y_{v\,max}$, m, and $k_{\bar{n}}$ stand for the slope of regression line, the maximum value of the measured signal obtained by regression analysis at maximum quantity of the analyzed substance m_{max} taken into account, the mass of the analyzed substance, and the value of statistical coefficient obtained by interpolation from the dependence on n for $\bar{n}$, respectively.

The measured results were not tested on their remoteness before calculating the regression straight line.

Results and discussion

The study of the reaction conditions for photometric determination of lanthanoides in pure solutions has shown that the medium of glycine buffer solution of pH = 2.6—pH = 3.1 is suited for the determination of lanthanoides with A III [1]. The minor quantities of some interfering elements could be screened by sulfosalicylic acid and α,α'-bipyridyl and thus this procedure was suited to photometric determination of some lanthanoides in simple metal systems (procedure A). However, this procedure failed in determining lanthanoides in some more complicated but practically important metal systems such as crude iron and especially different kinds of steel. Therefore it was necessary to find out a procedure for separation of cerium from the analyzed system. It appeared that Ce(III) could be separated by extraction in the form of the Ce(III) complex with phenylacetic acid. This complex may be extracted from the urotropine buffer solution like the complexes of U(VI) with phenylacetic acid, but under different reaction conditions [6].

Fig. 1 represents the extraction yield of the Ce(III)—phenylacetic acid complex. It was extracted from the pure urotropine buffer solutions into n-butyl alcohol, reextracted into HCl ($c = 0.1$ mol dm^{-3}) and determined with A III according to procedure A (procedure B). It is seen from Fig. 1 that the highest yield of extraction may be achieved under given conditions by using the urotropine buffer solution the pH value of which varies in the range 8.0 ± 0.5.

The position and shape of absorption bands of the Ce(III)—A III complex do not change in the analysis of pure solutions without regard whether procedure B or procedure A is used. The intensity of the maximum of the absorption band A_{max}(650 nm) is a linear function of Ce(III) up to the amount of 80 µg of Ce(III) in the analyzed solution. The calibration graph obtained by means of standard samples (after conversion to the cell length of 4.0 cm) may be expressed by the following equation

$$A_v(650 \text{ nm}) = (0.04307 \pm 0.00031)\{m_{Ce}\} - (0.107 \pm 0.018)$$

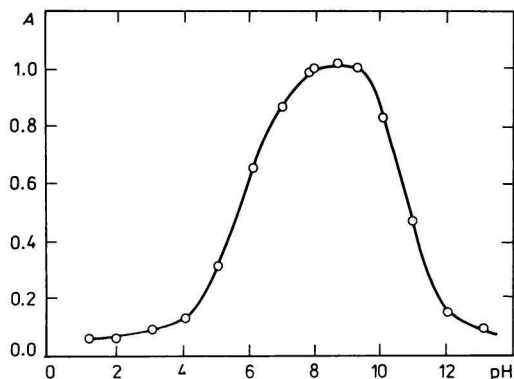$$n = 20; \quad R = 0.9970; \quad \Sigma\Delta^2 = 0.1147 \tag{1}$$

Fig. 1. Variation of extraction yield of the Ce(III)—phenylacetic acid complex with the pH value of urotropine solutions.

Quantity of 80 μg of Ce(III) was extracted into n-butyl alcohol and afterwards it was reextracted into 0.1 M-HCl. After reextraction Ce(III) was determined with arzenazo III at A_{max}(650 nm) in glycine buffer solution of pH = 2.7; length of the cell = 1.0 cm, $V = 25$ cm^3. Determination with respect to equally prepared solutions without cerium.

where A_v(650 nm) is the value of absorbance calculated by the method of least squares from the measured values, n is the total number of measurements, R is the coefficient of correlation, and $\Sigma\Delta^2$ is the sum of squared deviations between the measured and by the method of least squares calculated absorbances.

When microquantities of cerium were determined in multicomponent systems (crude iron, steel) by procedure B, it was sometimes possible to observe a change in intensity as well as shape of the absorption bands of the Ce(III)—A III complex. On the basis of our observations and confrontation of our results with the results presented in paper [7] dealing with separation of the complex of U(VI) with phenylacetic acid from multicomponent systems, we may conclude that the extraction of the Ce(III)—phenylacetic acid complex is not selective enough. For this reason, another operation, *i.e.* extraction of accidental interfering elements with cupferron was introduced into procedure B. Its aim was to eliminate the accidental interfering elements extractible with phenylacetic acid so that the present cerium remained in the analyzed solution. This objective was achieved if the pH value of the analyzed solution did not exceed pH = 2.5. Provided the contents of other interfering elements are not high after elimination of major components from the analyzed solution by n-amyl acetate (diethyl ether) or electrolysis and can be removed by extraction with cupferron, Ce(III) may be determined with A III immediately after this separation by using procedure A. However, we proceed in the most general case so that the medium high contents of interfering elements are extracted with cupferron (after extraction with n-amyl acetate, diethyl ether or preceded by electrolysis) and the complex of Ce(III)

containing phenylacetic acid is extracted with n-butyl alcohol from the urotropine buffer solution of pH = 8.0 ± 0.5. Then the organic phase is reextracted directly into the glycine buffer solution the pH value of which varies after reextraction in the range pH = 2.5—pH = 3.1 and Ce(III) is determined with A III (procedure C). the calibration graph for this procedure obtained by the use of standard samples (after conversion to the cell length of 4.0 cm) may be expressed by eqn (2)

$$A_v(650 \text{ nm}) = (0.04287 \pm 0.00029)\{m_{Ce}\} + (0.041 \pm 0.012)$$

$$n = 25; \quad R = 0.9984; \quad \Sigma\Delta^2 = 0.0807 \tag{2}$$

For comparing all three procedures (A, B, C), Fig. 2 represents the relationship between $A_{max}(650 \text{ nm})$ of the Ce(III)—A III complex and the pH value of glycine buffer solutions.

A comparison of the intensities of absorption bands (Figs. 1 and 2) reveals that the complex of Ce(III) containing phenylacetic acid is extracted from the uro-tropine buffer solution of pH = 8.0 ± 0.5 with the yield exceeding 90 %. A more exact value of the yield of extraction for the mass interval 4—80 μg of Ce(III) in the analyzed solutions may be obtained from the ratio of slopes of the linear relationships expressed by eqns (1) and (2) to the slope of the linear relationship
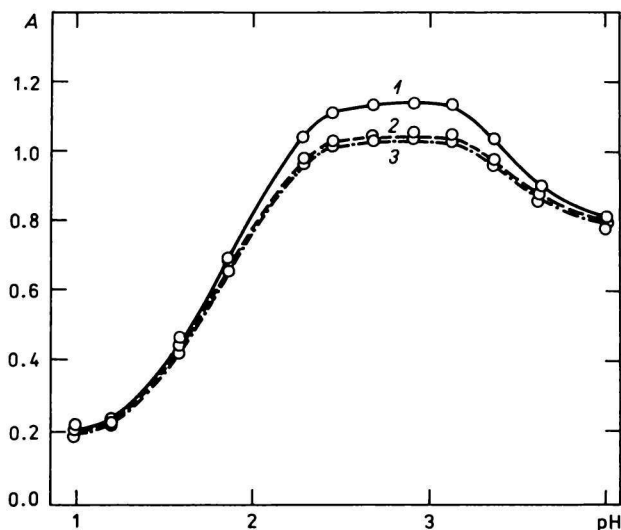

Fig. 2. Variation of the absorption maximum $A_{max}(650 \text{ nm})$ of the Ce(III)—arzenazo III complex with the pH value of glycine buffer solutions.
Quantity of 80 μg of Ce(III) in volume $V = 25 \text{ cm}^3$, length of the cell = 1.0 cm. Determination with respect to equally prepared solutions without cerium.
1. According to procedure A, taken from paper [1]; 2. Ce(III) extracted with phenylacetic acid according to procedure B; 3. Before extraction of Ce(III) with phenylacetic acid the interfering elements were extracted with cupferron according to procedure C.

obtained for direct determination ($\varrho = 0.04698$) and presented in paper [1]. It results from these comparisons that the extraction yield for Ce(III) with phenylacetic acid according to procedure B is 91.7 % and according to procedures B and C (Table 1), we may state that both procedures give practically equal yields. However, we must allege that procedure C is more universal than procedures A and B and simultaneously makes possible mutual confrontation of the results of analyses.

Table 1 contains the results of determination of cerium with arzenazo III and their statistical evaluation processed by different mathematical-statistical methods. For comparison, there are some values taken from paper [1] in this table. In order to clear up the influence of the use of different statistical relations, the precision and accuracy are graphically evaluated in Figs. 3 and 4.

It is obvious from these plots that the use of current statistical relationships gives nonmonotonic relations which do not enable us to estimate the width of tolerance zone. On the other hand, if we use the proposed relationships (denoted by index v), we obtain monotonic relation which averages the values of standard deviations and relative errors in dependence on concentration of the determined component.

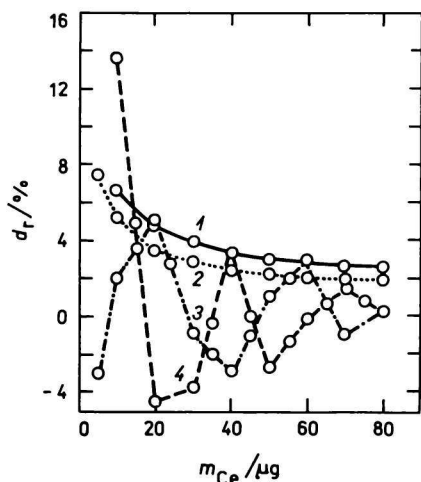Fig. 3. Variation of estimate of the relative error of determination d_r with quantity of the determined cerium.
1. $d_{r,v}$ for procedure B; 2. $d_{r,v}$ for procedure C;
3. $d_r(\bar{x})$ for procedure B; 4. $d_r(\bar{x})$ for procedure C.
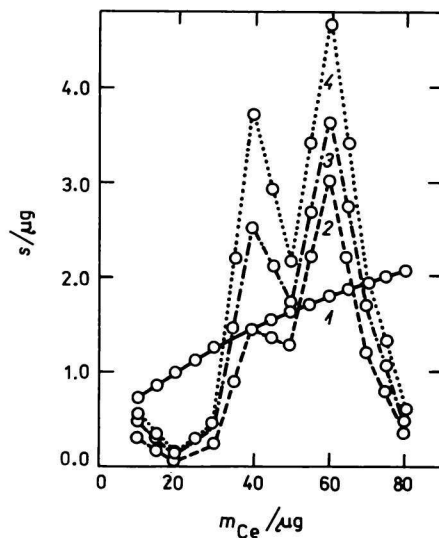
Fig. 4. Variation of estimate of the standard deviation s with quantity of cerium for procedure B.
1. s_v; 2. $s(\bar{x})$; 3. $s(x)$; 4. $s(R)$.

Table 1

Results of testing the determination of cerium with arzenazo III in standard solutions

Given $m_{Ce}/\mu g$	Procedure A				Procedure B				Procedure C			
	Determined $m_{Ce}/\mu g$	$s(\bar{x})$	$s_r(\bar{x})$	$d_r(\bar{x})$	Determined $m_{Ce}/\mu g$	$s(\bar{x})$ / $s(x)$ / $s(R)$ / s_v	$s_r(\bar{x})$ / $s_r(x)$ / $s_r(R)$ / $s_{r,v}$	$d_r(\bar{x})$ / — / — / $d_{r,v}$	Determined $m_{Ce}/\mu g$	$s(\bar{x})$ / $s(x)$ / $s(R)$ / s_v	$s_r(\bar{x})$ / $s_r(x)$ / $s_r(R)$ / $s_{r,v}$	$d_r(\bar{x})$ / — / — / $d_{r,v}$
80	81.39	1.392	1.74	0.26	80.23	0.315	0.39	0.29	80.34	1.279	1.60	0.43
						0.455	0.56			1.809	2.26	
						0.558	0.70			2.266	2.83	
						2.077	2.59	2.39		1.464	1.83	1.83
60	60.29	0.288	0.48	−0.22	59.83	2.660	4.43	−0.28	58.25	0.116	1.93	−2.92
						3.610	6.23			0.223	0.37	
						4.713	7.86			0.205	0.34	
						1.799	3.00	2.76		1.268	2.11	2.11
40	38.36	0.284	0.71	−4.11	41.35	1.448	3.62	3.38	38.76	0.864	2.16	−3.10
						2.508	6.27			1.502	3.75	
						3.635	9.09			1.765	4.41	
						1.469	3.67	3.37		1.035	2.59	2.59
20	20.31	0.164	0.82	1.56	19.10	0.005	0.03	−4.50	21.03	0.612	3.06	5.15
						0.009	0.04			1.060	5.30	
						0.012	0.06			1.194	5.97	
						1.038	5.19	4.77		0.732	3.66	3.66
10					11.35	0.271	2.71	13.50	10.19	0.266	2.66	1.90
						0.469	4.69			0.532	5.32	
						0.544	0.544			0.626	6.26	
						0.734	7.34	6.75		0.518	5.18	5.18

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Table 1 (Continued)

DETERMINATION OF CERIUM

Given m_{Ce}/µg	Procedure A				Procedure B				Procedure C			
	Determined m_{Ce}/µg	$s(\bar{x})$	$s_r(\bar{x})$	$d_r(\bar{x})$	Determined m_{Ce}/µg	$s(\bar{x})$ $s(x)$ $s(R)$ s_v	$s_r(\bar{x})$ $s_r(x)$ $s_r(R)$ $s_{r,v}$	$d_r(\bar{x})$ — — $d_{r,v}$	Determined m_{Ce}/µg	$s(\bar{x})$ $s(x)$ $s(R)$ s_v	$s_r(\bar{x})$ $s_r(x)$ $s_r(R)$ $s_{r,v}$	$d_r(\bar{x})$ — — $d_{r,v}$
4	4.60	0.100	2.50	15.00					3.87	0.491	9.83	−3.25
										0.982	19.64	
										0.957	19.13	
										0.366	7.31	7.31
50					48.60	1.230	2.46	−2.80	50.35	1.385	2.77	0.70
						1.739	3.48			1.959	3.92	
						2.162	4.32			2.455	4.90	
						1.642	3.28	3.02		1.157	2.30	2.30
30					28.86	0.253	0.84	−3.80	29.70	0.593	1.98	−1.00
						0.438	1.46			0.871	2.90	
						0.449	1.50			1.213	4.04	
						1.272	4.24	3.90		0.896	2.99	2.99
70					71.03	1.204	1.72	1.47	69.33	0.580	0.83	−0.96
						1.703	2.43			0.718	1.03	
						2.135	3.05			1.028	1.47	
						1.943	2.77	2.55		1.369	1.96	1.96

On the basis of these plots as well as the results presented in papers [6, 8], we may assert that the proposed relationships are convenient for the estimate of precision and accuracy.

By using the described procedures and relationships for calculating the precision and accuracy, the determinations of cerium in real samples were evaluated. The results are summarized in Table 2.

Table 2

Results of photometric determination of mass fraction of Ce(III) with arzenazo III in iron, steel, and some metals

No.	Material	Procedure					
		A		B		C	
1	Co—Ce	1.04	±0.012*	1.05	±0.012	1.05	±0.011
2	Co—Ce	0.261	±0.015*	0.262	±0.018		
3	Co—Ce	0.041	±0.002*	0.042	±0.002	0.041	±0.002
4	Cu—Ce	1.03	±0.02*	1.05	±0.02	1.05	±0.01
5	Cu—Ce	0.028	±0.013*			0.028	±0.010
6	Cu—Ce	0.041	±0.001*	0.041	±0.002		
7	Fe—Ce	0.006	±0.001	0.006	±0.0004	0.006	±0.0003
8	Fe—Ce	0.0009	±0.0003	0.0010	±0.0002	0.0011	±0.0001
9	crude Fe—Ce			0.8	±0.02	0.8	±0.02
10	crude Fe—Ce			0.5	±0.003	0.05	±0.002
11	crude Fe—Ce			0.007	±0.001	0.008	±0.0005
12	steel—Ce			0.8	±0.02	0.8	±0.02
13	steel—Ce			0.05	±0.002	0.05	±0.002
14	steel—Ce			0.002	±0.0005	0.003	±0.0002

* Results are taken from paper [1].

In conclusion, we may state that the developed procedures (B and C) move the limit of determination of cerium in pure iron and its simple alloys by 0.5 decimal order towards its lower mass fractions in comparison with procedure A [1], *i.e.* to $w > 5 \times 10^{-4}$ %. The importance of procedures B and C consists especially in the fact that they enable us to determine cerium in such complicated and practically important systems as crude iron and steel provided $w > 1 \times 10^{-3}$ %.

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