Chemistry of
Metals and Alloys

Chem. Met. Alloys 8 (2015) 10-15
Ivan Franko National University of Lviv
www.chemetal-journal.org

Selection of reagents for voltammetric analysis of samples containing simultaneously Al(III), Ga(III), In(III), Sc(III) or *REE*(III)

Liliya DUBENSKA[1]*, Sofija TVORYNSKA[1], Solomiya PYSAREVSKA[2], Julija RAK[1]

[1] *Department of Analytical Chemistry, Ivan Franko National University of Lviv,*
Kyryla i Mephodia St. 6, 79005 Lviv, Ukraine
[2] *Department of Life Safety, Ivan Franko National University of Lviv,*
Doroshenka St. 41, 79000 Lviv, Ukraine
** Corresponding author. Tel.: +380 32 2394631; e-mail: dubenskyy@gmail.com*

Received February 19, 2015; accepted June 24, 2015; available on-line September 1, 2015

The possibility of simultaneous polarographic determination of two metals with azo dyes (eriochrome blue SE, kalces, eriochrome red B, eriochrome black T) was studied. The following metals were investigated: Al(III), Sc(III), Ga(III), In(III), and *REE*(III). The optimal conditions for the determination of different combinations of these metals were established. The main factor determining the possibility of simultaneous analysis is the pH of the medium, and appropriate values of pH for the determination of different pairs of *M*(III) by linear sweep polarography are proposed. Other factors, like the amount of azo dye, were also analyzed. The polarographic methods elaborated here were used in the analysis of alloys. The results obtained by the polarographic method were in good agreement when different azo dyes were used, and with the results obtained by independent spectrophotometric methods. The reported polarographic methods can be used for precise and accurate simultaneous determination of two metals with similar properties and is twice faster than known spectrophotometric methods, which require a preliminary separation step.

Rare earth elements / Alloy / Azo dye / Polarography / Spectrophotometry

Introduction

Al(III), Ga(III), In(III), Sc(III), and *REE*(III) are widely used in different fields: from thermonuclear reactors to microelectronics, from high-power magnets to high-temperature ceramics, from lasers, luminophores, or emissive materials to microfertilizers. Consequently, an important and at the same time difficult goal of analytical chemistry is to develop new methods for the analysis of complex samples. Several reviews and monographs [1-4] are devoted to this problem. Inductively coupled plasma mass spectrometry is a high-performance method for this purpose, but it is very laborious and expensive. Spectrophotometric methods utilizing different dyes (triphenylmethane, xanthene, and azodyes) are the simplest, and still the most popular methods for the determination of Al(III), Ga(III), In(III), Sc(III), or *REE*(III). However, Al(III), Ga(III), In(III), Sc(III), and *REE*(III) react with the same reagents under approximately the same conditions, resulting in similar products. The absorption spectra of these products reveal substantial overlap. Hence, in most cases preliminary separation must be performed when analyzing a mixture of these analytes. The pairs Al(III) and Sc(III), Al(III) and Ga(III), Ga(III) and In(III) cause special problems in analytical chemistry.

Electrochemical methods are less common for the determination of these metals. However, linear sweep polarography is a selective and sensitive method for the determination of metals when electroactive complexing agents are used [5,6]. Particularly azo dyes have found successful utilization in polarographic methods [7-9]. Azo dyes contain an azo group, which is able to be reduced in the range of polarization of a mercury electrode. This causes the electroactivity of the azo dyes. In addition they form complexes with different analytes of different composition and stability. The ligand in such complexes is reduced at different potentials. The difference between the reduction potentials of the complexes allows quantitative analysis of several metals without previous separation [7-9]. For instance, Poperechnaja *et al.* [10] reported the possibility of simultaneous determination of In(III) and *REE*(III), but the authors only investigated optimal conditions of *REE*(III) determination. A similar approach was used in this work.

Experimental

Apparatus

Voltammetric measurements were carried out on a digital device equipped with a personal computer and a temperature-controlled three-electrode cell, volume 10 ml. An indicator dropping mercury electrode, a saturated calomel reference electrode, and a platinum wire auxiliary electrode were used. The dropping mercury electrode had the following characteristics: $m = 4.6 \cdot 10^{-4}$ g/s and $\tau_k = 10.8$ s.

The pH of the solutions was measured potentiometrically with a MV 870 DIGITAL-pH-MESSGERÄT pH-meter. Spectrophotometric measurements were carried out on a SPEKOL-11 spectrocolorimeter, using cells with $l = 1$ cm.

Chemicals

The pH values were adjusted by acetate, ammonium-acetate and ammonium buffer solutions. Stock solutions of $1 \cdot 10^{-2}$ M M(III) were prepared by dissolving the appropriate quantity of metal containing 99.999 % of the major substance in a mixture of conc. HCl and conc. HNO_3 (c.p. grade). The solution of metal was standardized complexometrically.

Stock standard $1 \cdot 10^{-3}$ M solutions of azo dyes were prepared by dissolving appropriate quantities of reagents (analytical grade) in an aqua-ethanol mixture, where the ethanol content was 50 % for eriochrome black T (EBT), 40 % for eriochrome red B (ERB), 25 % for eriochrome blue SE (EBSE), and 10 % for kalces (Klc). These solutions were standardized spectrophotometrically. Working solutions were prepared by diluting stock solutions with doubly distilled water. Alloys prepared at the Department of Inorganic Chemistry of the Ivan Franko National University of Lviv were used for the analysis.

Purified argon was used to remove dissolved oxygen.

Procedure

All the solutions were prepared by mixing the constituents in the following order: buffer solutions, solutions of azo dyes, M_1(III)-M_2(III) ions solution. The working solutions were introduced into the cell and then they were deoxygenated with argon for 10 min.

Results and discussion

The following azo dyes were used in the work: eriochrome blue SE (EBSE), kalces (Klc), eriochrome red B (ERB) and eriochrome black T (EBT). These dyes have earlier been studied as complexing reagents for Sc(III), Ga(III), and *REE*(III). The investigations indicated the possibility of sensitive determination of metals with these azo dyes.

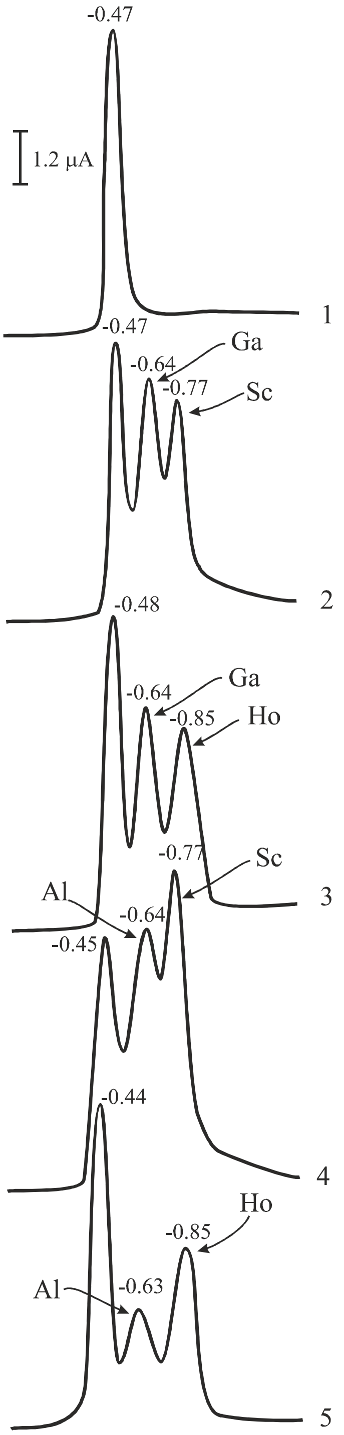

Fig. 1 Polarograms in EBSE solutions without metal ions (1); with Ga(III) and Sc(III) (2); with Ga(III) and Ho(III) (3); with Al(III) and Sc(III) (4); with Al(III) and Ho(III) (5), $C_{EBSE} = 4 \cdot 10^{-5}$ M, $C_{M(III)} = 8 \cdot 10^{-6}$ M, $V = 0.5$ V/s, pH 7.5, polarization from –0.1 to –1.2 V.

Fig. 1 shows polarograms of EBSE solutions containing two different M(III) ions. Arrows indicate the peaks due to ligand reduction in complexes with the indicated M(III) ion. The most important feature affecting the polarographic characteristics is the pH.

Simultaneous determination of two metals is possible when, at an appropriate pH, the difference between the reduction peak potentials is maximal. The current and difference between the potentials corresponding to the reduction of the complexes, change when the pH changes (Fig. 2).

Similar dependences were obtained for Klc and EBT. At pH 4.0-10.5, the reduction peaks of the ERB complexes with Al(III), Ga(III), or Sc(III), and those of *REE*(III) overlap, which does not allow measuring the potential and current for these pairs.

The results of the studies are summarized in Table 1, which gives the optimal pH for maximal separation of the reduction peaks of different metal complexes.

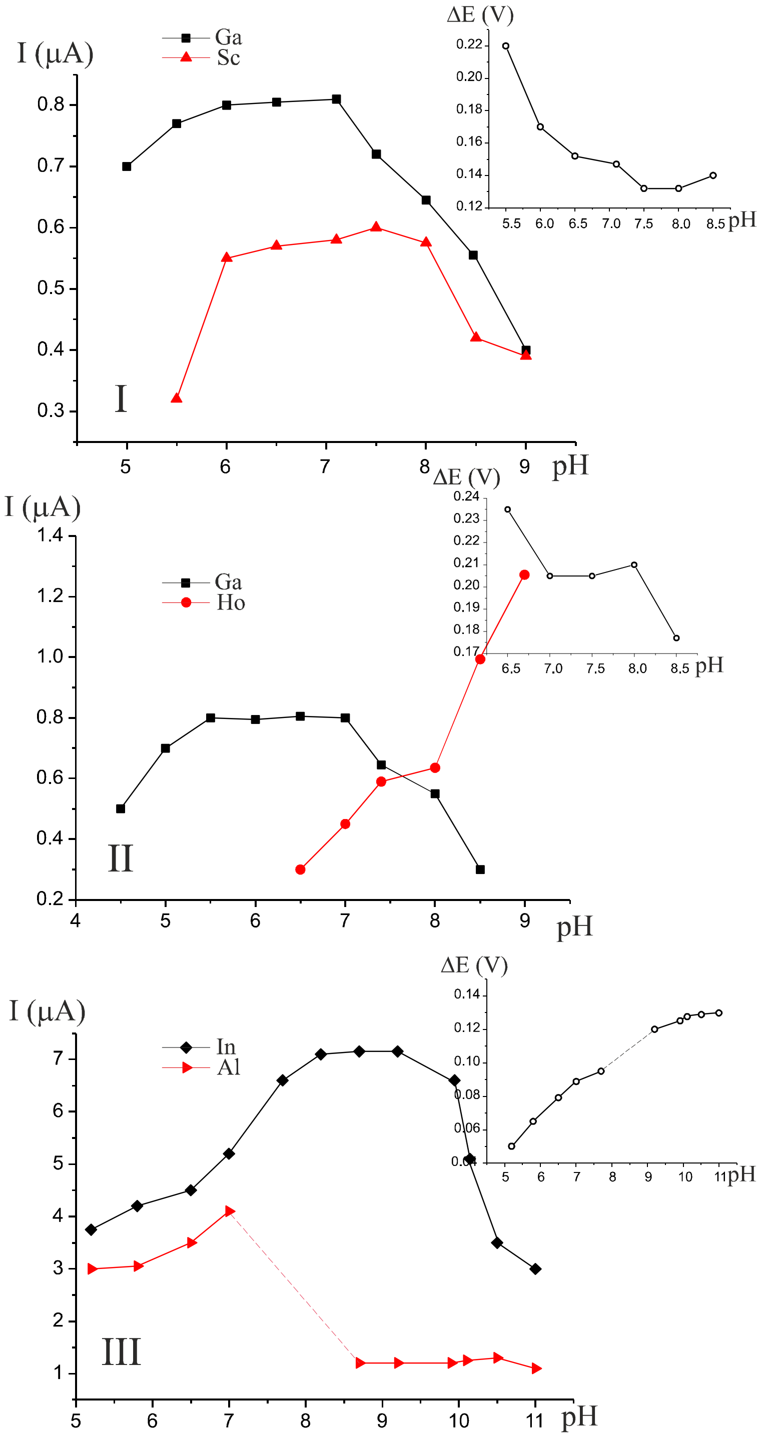

Fig. 2 Dependence of the current (μA) and the difference between the reduction peak potentials (V) of EBSE complexes with Ga(III) and Sc(III) (I); Ga(III) and Ho(III) (II); In(III) and Al(III) (III) on the pH of the medium.

Table 1 Conditions to be fulfilled for the simultaneous determination of two metal ions with azo dyes, $C_{\text{azo dye}} = 4\cdot10^{-5}$ M, $C_{M(\text{III})} = 8\cdot10^{-6}$ M.

Azo dye	M_1(III) and M_2(III)	Optimal pH	$-E^{к}_{p}$, V	Background electrolyte
EBSE	Ga(III) and Sc(III)	7.0-8.0	0.61 0.74-0.77	CH_3COONH_4
	Al(III) and Sc(III)	6.5-7.5	0.63-0.64 0.77	CH_3COONH_4
	Al(III) and Ho(III)	6.5-7.5	0.61-0.62 0.83-0.85	CH_3COONH_4
	Ga(III) and Ho(III)	7.0-8.5	0.61-0.64 0.83-0.85	$NH_4Cl + NH_3$
Klc	Ga(III) and Sc(III)	4.5-5.5	0.40-0.48 0.56-0.63	$CH_3COONa + CH_3COOH$
	Al(III) and Ho(III)	8.5	0.73 0.80	$NH_4Cl + NH_3$
	Ga(III) and Ho(III)	8.0	0.65 0.79	$NH_4Cl + NH_3$
EBT	Sc(III) and Ga(III)	6.0-7.0	0.67-0.72 0.52-0.61	CH_3COONH_4
	Sc(III) and Al(III)	6.0	0.66 0.61	CH_3COONH_4
	Al(III) and Ho(III)	7.9-8.5	0.67 0.76-0.79	$NH_4Cl + NH_3$
	Sc(III) and Ho(III)	8.0-9.0	0.61-0.66 0.76-0.80	$NH_4Cl + NH_3$
ERB	In(III) and Al(III)	6.0-7.0	0.80-0.85 0.88-0.95	CH_3COONH_4
	In(III) and Ho(III)	9.5-10.5	0.85-0.88 0.92-0.99	$NH_4Cl + NH_3$
	In(III) and Sc(III)	8.5	0.85 0.95	$NH_4Cl + NH_3$

The effect of the concentrations of M_1(III) and M_2(III) ions on the voltammetric characteristics of the M_1(III)−M_2(III)−EBSE and M_1(III)−M_2(III)−Klc systems was studied. The concentration of M_1(III) was varied from $8\cdot10^{-7}$ to $2\cdot10^{-5}$ M, while the concentration of M_2(III) was held constant and equal to $8\cdot10^{-6}$ M. The increase of the concentration of one of the metals leads to an increase of its complex reduction peak, while the complex reduction peak of the metal, the concentration of which remains constant, does not change till the moment the azo dye lacks (Fig. 3). The reduction peak of the free ligand decreases. Parameters of the calibration curves obtained at constant concentrations of both EBSE and one of the metals at optimal conditions are presented in Table 2. The parameters of the calibration curve, the correlation coefficient (R) and the limit of quantitation for M_1(III), were estimated from the obtained calibration curves according to [11].

The peculiarities of the reduction of M_1(III) and M_2(III) azo dye complexes allow simultaneous determination of metals. Hence, new methods have been elaborated. Analysis of alloys was used to evaluate the accuracy and precision of the methods. In parallel, the alloys were analyzed by known spectrophotometric methods: Al(III) with eriochrome cyanine R, Ga(III) with glycine cresol red, In(III) with 4-(2-pyridylazo)resorcinol, and *REE*(III) with arsenazo III [12]. The time needed for the spectrophotometric analysis was twice as long, in comparison with the polarographic method. In the case of the spectrophotometric methods, In(III) must previously be separated from *REE*(III).

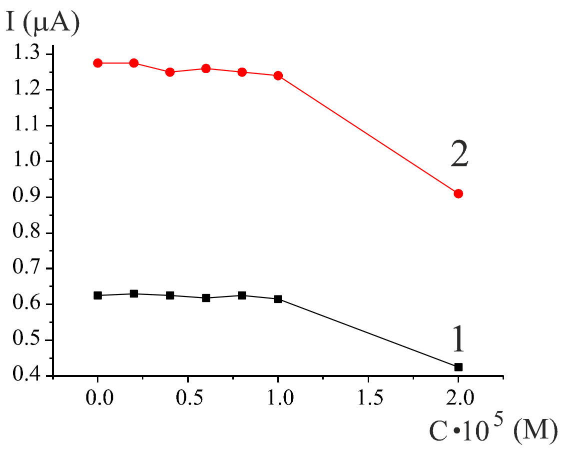

Fig. 3 Dependence of the reduction peak current for Sc(III) (1) and Ga(III) (2) on the concentration of Ga(III) (1) and Sc(III) (2) $C_{\text{azo dye}} = 8\cdot10^{-5}$ M, $C_{M(\text{III})}$ = cst = $1\cdot10^{-5}$; pH 5.0.

Table 2 Metrological characteristics of the determination of M_1(III) in the presence of M_2(III) ($C_{M_2\text{(III)}} = 8\cdot10^{-6}$ M)) with EBSE at the conditions defined in Table 1.

M_1(III) of variable concentration	M_2(III) of constant concentration	Parameters of the calibration curve I = a + bC		Correlation coefficient R	Limit of quantitation for M_1(III), M
		a	b·10^4		
Sc(III)	Al(III)	0.13	7.2	0.9977	$3.6\cdot10^{-6}$
Sc(III)	Ga(III)	0.17	4.5	0.9823	$5.8\cdot10^{-6}$
Ga(III)	Sc(III)	0.51	7.2	0.9634	$4.3\cdot10^{-6}$
Ga(III)	Ho(III)	0.55	4.5	0.9728	$3.8\cdot10^{-6}$
Ho (III)	Ga(III)	0.46	2.4	0.9829	$7.6\cdot10^{-6}$
Ho(III)	Al(III)	0.46	5.3	0.9898	$3.9\cdot10^{-6}$
Al(III)	Ho(III)	0.33	3.6	0.9629	$6.3\cdot10^{-6}$
Al(III)	Sc(III)	0.46	2.3	0.9848	$4.8\cdot10^{-6}$
Eu(III)	Al (III)	0.34	4.4	0.9840	$4.9\cdot10^{-6}$

Procedure for the analysis of alloys

Samples of alloys (~0.01-0.03 g) were accurately weighed and then dissolved in 3 ml of conc. HCl. The solutions were heated to form wet salts. Then the residue was dissolved in 3 ml of conc. HCl and was diluted to 100 ml with doubly distilled water.

A background electrolyte with pH according to Table 1, an azo dye solution with a final concentration in the flask of $8\cdot10^{-5}$-$1\cdot10^{-4}$ M, and an aliquot of analyzed solution, were placed into a 25 ml flask and diluted with doubly distilled water to the mark. Then the prepared solutions were introduced into the cell and deoxygenated with argon. The voltammograms were recorded by making potential sweeps from –0.1 to –1.4 V at a sweep rate of 0.5 V/s.

The form of the polarograms indicates if the volume of the aliquot is correct, *i.e.* the polarogram must contain the peak of the free ligand. This is the evidence of sufficient excess of reagent. If this is not the case, the aliquot of the studied solution must be decreased, or the stock solution of the probe must be diluted.

The content of M_1(III) and M_2(III) in objects with a complex matrix should be determined by the method of standard additions to take into account the mutual effect of the components of the matrix. Fig. 4 shows the polarogram obtained in a solution of EBSE with an aliquot of a Ho−Zn−Al alloy solution.

The results of the determination of metal pairs in alloys of different compositions are shown in Table 3. The results obtained by the polarographic method are in good agreement when different azo dyes are used, and with the results obtained by the independent spectrophotometric method [12]. This conclusion results from the values of the Student's t-criteria: $t_{calc} < t(0.95;2)$ [11]. However, the content of Sm(III) in the SmGa alloy, determined by two independent methods, was less than the nominal content. Polarography and spectrophotometry gave approximately the same result for the Sm(III) content, and the difference can be explained by losses during the different stages of the preparation of the alloy.

Conclusions

The optimal conditions for simultaneous polarographic determination of element pairs, which are analytical analogues of Sc(III), Ga(III), Al(III), In(III), and *REE*(III), do not coincide with the optimal conditions for the determination of the individual metals. The best results for simultaneous determination of the Sc(III)–Ga(III) pair were achieved with EBSE, Klc and EBT; for the Sc(III)–Al(III) pair with EBSE and EBT; for the Sc(III)–*REE*(III) pair with EBT; for the Al(III)–*REE*(III) pair with EBSE and Klc; and for the Ga(III)–*REE*(III) pair with EBSE and Klc.

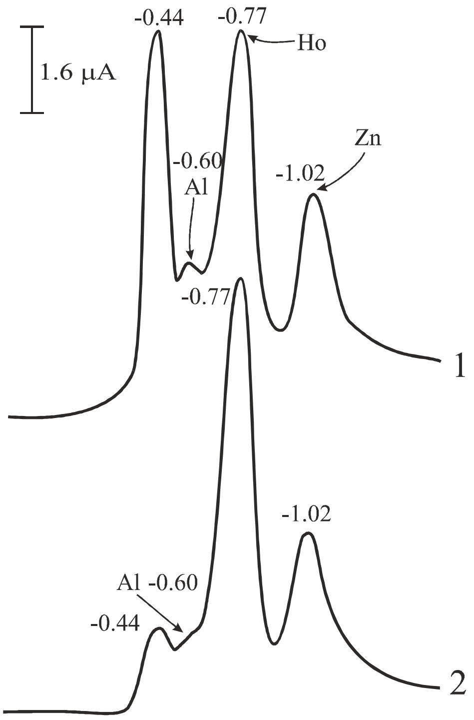

Fig. 4 Polarograms in EBSE solution with an aliquot of Ho−Zn−Al alloy (1) and with a standard solution of Ho(III) (2), $C_{\text{Klc}} = 8\cdot10^{-5}$ M, $C_{\text{Ho(III)}} = 4\cdot10^{-6}$ M, V = 0.5 V/s, pH 7.5.

Table 3 Results of simultaneous determination of *M*(III) in alloys at the conditions defined in Table 1 ($n = 3$, $P = 0.95$).

Sample	Sample mass, g	Content of *M*(III), calculated according to the formula, %	Found polarographically (PG), $X \pm \Delta X$, %		Standard deviation, S		Found spectrophotometrically (SP), %	Student's *t*-criteria, comparison of results		
			Klc	EBSE	Klc	EBSE		PG	SP with Klc	SP with EBSE
Determination of *REE*(III)										
$Ho_{15}Zn_{70}Al_{15}$	0.0310	33.2	32.0±1.7	32.7±2.2	0.68	0.90	30.9	2.03	2.80	3.46
$Yb_5Zn_{50}Al_{45}$	0.0294	16.2	15.9±1.6	15.1±2.3	0.63	0.95	17.3	3.90	3.84	4.00
	0.0175	16.2	15.7±0.5	15.5±0.6	0.19	0.22	16.0	3.05	2.73	3.92
$Yb_{10}Zn_{20}Al_{40}$	0.0279	42.1	41.8±1.9	40.1±3.4	0.75	1.40	43.2	2.45	3.23	3.89
$Sm_{17}Ge_{17}In_{66}$	0.0452	22.5	22±2 [a]		0.82 [a]		23.6	–	3.80	
$Y_{40}Si_{40}In_{20}$	0.1083	51.0	51.8±0.6 [a]		0.26 [a]		52.2	–	2.66	
SmGa	0.1835	68.2	30±3	31.8±1.9	1.22	0.75	32.7	3.23	3.80	2.10
$SmIn_2$	0.0362	39.5	40±3 [a]		1.00 [a]		42.3	–	3.98	
Determination of Al(III)										
$Ho_{15}Zn_{70}Al_{15}$	0.0310	5.4	5.0±0.3	5.2±0.4	0.12	0.14	4.9	4.80	1.44	3.71
$Yb_5Zn_{50}Al_{45}$	0.0294	22.8	19.0±0.9	19.3±0.9	0.35	0.38	19.6	3.66	2.97	1.36
$Yb_{10}Zn_{20}Al_{40}$	0.0279	26.3	26.7±0.7	26.9±1.1	0.28	0.45	26.3	0.98	2.47	2.31
Determination of In(III) [a]										
$Sm_{17}Ge_{17}In_{66}$	0.0452	66.7	66±3		1.20		67.5	–	2.98	
$Y_{40}Si_{40}In_{20}$	0.1083	32.9	32±2		0.88		33.2	–	2.19	
$SmIn_2$	0.0362	60.5	60±2		0.95		62.0	–	4.19	
Determination of Ga(III)										
SmGa	0.1835	31.8	30±3	32.3±1.6	1.40	0.71	32.7±1.5	3.30	2.50	0.80

[a] with ERB.

ERB is suitable for simultaneous polarographic determination of the investigated *M*(III) pairs, when one of the metals is In(III).

The studied azo dyes cannot be used for simultaneous determination of Ga(III) and Al(III).

References

[1] R.T. Prasada, V.M. Biju, *Crit. Rev. Anal. Chem.* 30 (2000) 179-220.

[2] M.R. Buchmeiser, *Anal. Chem.* 20 (2001) 161-181.

[3] L.N. Komissarova, *Inorganic and Analytical Chemistry of Scandium*, Editorial URSS, Moscow, 2001, p. 512 (in Russian).

[4] Y. Chung, Ch-W. Lee, *J. Electrochem. Sci. Technol.* 4 (2013) 1-18.

[5] P.D. Schumacher, P.D. Chowdhury, J.L. Doyle, J.O. Schenk, S.B. Clark, *Anal. Chem.* 32 (2013) 159-171.

[6] L.O. Dubenskaya, G.D. Levitskaya, N.P. Poperechnaya, *J. Anal. Chem.* 60 (2005) 304-309.

[7] L. Dubenska, H. Levytska, N. Poperechna, *Talanta* 54 (2001) 221-231.

[8] S. Pysarevska, L. Dubenska, N. Shajnoga, H. Levytska, *Chem. Met. Alloys* 2 (2009) 194-201.

[9] S. Pysarevska, L. Dubenska, I. Spanik, Ya. Kovalyshyn, S. Tvorynska, *J. Chem.* 2013 (2013) 853763.

[10] N.P. Poperechnaja, H.D. Levytskaja, M. Bohdan, *Zav. Lab., Diagnos. Mater.* 68 (2002) 26-29.

[11] K. Doerffel, *Statistik in der analytischen Chemie*, Deutscher Verlag für Grundstoffindustrie GmbH, Leipzig, 1990, p. 268.

[12] Z. Marchenko, *Photometric Determination of Elements*, Mir, Moscow, 1971, pp. 501 (in Russian).