

**EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION  
OF SELECTED RARE EARTH ELEMENTS  
IN THE PRESENCE OF OTHER IN THE SYSTEM:  
Ln<sup>3+</sup>-HEXAAZA-18-CROWN-6-ERYTHROSINE A**

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The spectrophotometric determination of some lanthanides in the presence of other cations, based on solvent extraction of the ion-associates formed between the Ln<sup>3+</sup>-hexaaza-18-crown-6 complexes and erythrosine A, is proposed. By use of masking agents, the method can be applied to the determination of 0.02–1% of Pr(III), Nd(III), Sm(III), Eu(III), Gd(III) and Tb(III) in the presence of a mixture of heavy lanthanides, Y(III), Ga(III), Sc(III), Al(III) and alkaline earth metal cations.

Zaproponowano spektrofotometryczną metodę oznaczania niektórych lantanowców wobec innych kationów, opartą na ekstrakcji asocjatu jonowego utworzonego między kompleksem Ln<sup>3+</sup>-hexaaza-18-korona-6 i erytrozyną A. Przy użyciu substancji maskujących metoda może być stosowana do oznaczania od 0,02 do 1% Pr(III), Nd(III), Sm(III), Eu(III), Gd(III) i Tb(III) wobec sumy lantanowców ciężkich, Y(III), Ga(III), Sc(III), Al(III) oraz kationów metali ziem alkalicznych.

Individual lanthanides in pure solution can easily be determined spectrophotometrically, but because of the poor selectivity of these methods, only group determinations (of the total light or heavy lanthanides) are possible for their mixtures. The ternary systems available [1–9] are more sensitive, but their selectivity still remains unsatisfactory.

Our extraction study presented recently [10] of the lanthanide–hexaaza-18 crown-6–erythrosine A system showed that some selectivity is achievable through effect of hydroxide, and samarium was determined in the presence of yttrium and the heavy lanthanides. In this work an extension of the system is proposed to cover determination of Eu<sup>3+</sup>, Sm<sup>3+</sup>, Pr<sup>3+</sup>, Nd<sup>3+</sup> or Gd<sup>3+</sup> in the presence of heavy lanthanides as well as Y<sup>3+</sup>, Sc<sup>3+</sup>, Ga<sup>3+</sup>, Al<sup>3+</sup> and alkaline earth metal ions.

## EXPERIMENTAL

### Reagents and apparatus

The hexaaza-18-crown-6-3H<sub>2</sub>SO<sub>4</sub> (HA18C6), erythrosine A and lanthanides solution were prepared as described earlier [10]. Gallium and aluminium stock solutions (0.1 mol l<sup>-1</sup>) were prepared by dissolving the metal in concentrated hydrochloric acid, in quartz flasks, evaporating the acid, taking up the salt in water and alkalinizing it to pH ~ 12 with 0.1 mol l<sup>-1</sup> sodium hydroxide.

Sulphosalicylic acid solution, 1×10<sup>-2</sup> mol l<sup>-1</sup> was prepared by dissolving the required mass in water and alkalinizing to pH = 11 with 0.1 mol l<sup>-1</sup> sodium hydroxide.

EDTA solution, 5×10<sup>-2</sup> mol l<sup>-1</sup> was prepared by dissolving the required amount in water and alkalinizing to pH = 11 with 0.1 mol l<sup>-1</sup> sodium hydroxide.

The working solutions were prepared by diluting the stock solutions with water.

Chloroform used was purified by distillation (fraction 60–62°C).

The other reagents were of analytical grade, and were used without preliminary purification.

The water used for preparation of the solutions was doubly distilled in a quartz apparatus.

The absorbance measurements were made with a Zeiss M 40 spectrophotometer and 10 mm path-length in glass cells.

### Procedure for determination of Ln<sup>3+</sup>

Transfer a 1 ml portion of test solution containing no more than 1.6 µg of lanthanide (Ln<sup>3+</sup>) and an amount of any of the interfering cations not exceeding the tolerance limit into each of five polyethylene separatory funnels and add 0, 0.1, 0.2, 0.3, and 0.4 ml of 5×10<sup>-5</sup> mol l<sup>-1</sup> standard Ln<sup>3+</sup> solution. Next, add to all funnels 0.5 ml of 5×10<sup>-3</sup> mol l<sup>-1</sup> HA18C6 for determination of Ln<sup>3+</sup> in the presence of heavy lanthanides and yttrium or of Ga<sup>3+</sup> and 1.5 ml of 1×10<sup>-4</sup> mol l<sup>-1</sup> HA18C6 for determination in the presence of Al<sup>3+</sup> and Sc<sup>3+</sup>, and then alkalinize to pH ~ 11.0 with 0.1 mol l<sup>-1</sup> sodium hydroxide.

Leave the solution for 2 h so that the complexes can form. Then, add to each funnel 1.5 ml of 1×10<sup>-4</sup> mol l<sup>-1</sup> erythrosine A and enough sodium hydroxide to give the required pH. Finally dilute with water to 5 ml.

Shake this solution with 5 ml of chloroform for 5 min, then centrifuge for 5 min at 2000 rpm. Measure the absorbance of the chloroform phase against a reagent blank at λ<sub>max</sub> = 550 nm. Determine the Ln<sup>3+</sup> content in the sample solution from the standard addition graph.

### Procedure for determination of Ln<sup>3+</sup> in the presence of alkaline earth metals

Transfer 1 ml portion of sample containing no more than 1.6 µg of Ln<sup>3+</sup>, 100 µg of Ca<sup>2+</sup>, 200 µg of Sr<sup>2+</sup> and 300 µg of Ba<sup>2+</sup> into each of four polyethylene separatory funnels and add 0, 0.1, 0.2, and 0.3 ml of standard Ln<sup>3+</sup> solution (5×10<sup>-5</sup> mol l<sup>-1</sup>) to separate funnels. To each funnel add 0.5 ml of 1×10<sup>-2</sup> mol l<sup>-1</sup> sulphosalicylic acid and 0.5 ml 1×10<sup>-3</sup> mol l<sup>-1</sup> HA18C6. Raise the pH to about 11 with 0.1 mol l<sup>-1</sup> sodium hydroxide. After 2 h, add 1.5 ml of 1×10<sup>-4</sup> mol l<sup>-1</sup> erythrosine A and 1 ml of 5×10<sup>-2</sup> mol l<sup>-1</sup> EDTA and water to make up to the total volume of 5 ml. Complete the determination as above.

## RESULTS AND DISCUSSION

The ternary coloured system Ln<sup>3+</sup>-HA18C6-E<sub>A</sub> where Ln<sup>3+</sup> = Pr<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup> or Tb<sup>3+</sup> has a molar absorptivity of ε = 1.36×10<sup>5</sup> l mol<sup>-1</sup> cm<sup>-1</sup>, and the calibration graph A = f(c) is linear over the range 0–5×10<sup>-6</sup> mol l<sup>-1</sup>, allowing determination of these elements at the 0.05 ppm level.

Formation of the Ln<sup>3+</sup>-HA18C6 complex is fastest for the first and last cations in the rare earth series. The efficiency of extraction of particular lanthanides depends on the sodium hydroxide concentration. In 0.1 mol l<sup>-1</sup> sodium hydroxide medium, Y<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup>, Yb<sup>3+</sup> and Lu<sup>3+</sup> are scarcely extracted at all, whereas the

extraction of  $\text{La}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Tb}^{3+}$  remains almost unchanged [10].

The determination of  $\text{Sm}^{3+}$  presented earlier [10] indicated the usefulness of this system for the determination of  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Tb}^{3+}$  in the presence of mixture of heavy lanthanides and yttrium and also in the presence of  $\text{Sc}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$  and alkaline earth metals. The results of such determinations are discussed below.

### Determination of $\text{Pr}^{3+}$ , $\text{Nd}^{3+}$ , $\text{Sm}^{3+}$ , $\text{Eu}^{3+}$ , $\text{Gd}^{3+}$ and $\text{Tb}^{3+}$ in the presence of heavy lanthanides

The results of determinations are presented in table 1.

**Table 1.** The results of determinations of  $\text{Eu}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Tb}^{3+}$  ( $n = 7$ ) and  $\text{Sm}^{3+}$  ( $n = 8$ ) in a solution containing 25.5  $\mu\text{g}$  of a mixture of  $\text{Ho}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Lu}^{3+}$

Determined $\text{Ln}^{3+}$	Introduced $\text{Ln}^{3+}$ , $\mu\text{g}$	Found $\text{Ln}^{3+}$ , $\mu\text{g}$	Standard deviation $s$	Relative standard deviation $s_r$ , %
Eu	0.38	0.37	0.026	7
Pr	0.35	0.36	0.029	8
Nd	0.36	0.36	0.018	5
Gd	0.39	0.38	0.027	7
Tb	0.39	0.39	0.020	5
Sm	0.37	0.36	0.022	6
	1.125	1.09	0.110	10
Sm*	1.125	1.125	0.124	11

\*51  $\mu\text{g}$  – amount of heavy lanthanides.

The concentration range of determined  $\text{Ln}^{3+}$  is independent of the nature of analyzed cation because they are characterized by this same molar absorptivity and linearity of calibration graph. Most of presented results were obtained in presence of 25.5  $\mu\text{g}$  of the mixture of heavy lanthanides so up to 1% of  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$  or  $\text{Tb}^{3+}$  can be determined in heavy lanthanides. The amount of heavy lanthanides is limited by precipitation of their hydroxides, but this amount can be increased up to 51  $\mu\text{g}$  as it is indicated by example for  $\text{Sm}^{3+}$  (Table 1). Because the determined amounts are at trace level, the precision obtained seems to be satisfactory.

### Determination of $\text{Pr}^{3+}$ , $\text{Nd}^{3+}$ , $\text{Sm}^{3+}$ , $\text{Eu}^{3+}$ , $\text{Gd}^{3+}$ and $\text{Tb}^{3+}$ in yttrium

Yttrium, which is not a lanthanide, shows great similarity to  $\text{Ln}^{3+}$  in the used extraction system. Yttrium is masked by hydroxyl ions, similarly to heavy lanthanides, what gives good possibilities for the determination of  $\text{Ln}^{3+}$ . The optimum conditions for  $\text{Ln}^{3+}$  determination in yttrium is 0.5 mol  $\text{l}^{-1}$  sodium hydroxide. This alkalinity allows for  $\text{Ln}^{3+}$  determination in the presence of 45  $\mu\text{g}$   $\text{Y}^{3+}$ . The results presented in Table 2 indicate satisfactory precision of the method.

**Table 2.** The results of determinations of  $\text{Ln}^{3+}$  in a solution containing  $45 \mu\text{g}$  of  $\text{Y}^{3+}$  ( $n = 7$ , except for  $\text{Sm}^{3+}$   $n = 5$ )

Determined $\text{Ln}^{3+}$	Introduced $\text{Ln}^{3+}$ , $\mu\text{g}$	Found $\text{Ln}^{3+}$ $\mu\text{g}$	Standard deviation $s$	Relative standard deviation $s_r$ , %
Sm	0.226	0.263	0.039	15
	1.053	1.053	0.063	6
	1.503	1.503	0.030	2
Eu	0.38	0.39	0.035	9
Nd	0.36	0.35	0.024	7
Pr	0.35	0.36	0.025	7
Gd	0.39	0.38	0.030	8
Tb	0.39	0.38	0.034	9

### Determination of $\text{Eu}^{3+}$ in the presence of $\text{Sc}^{3+}$

Europium was chosen as a pilot ion to examine a possibility of  $\text{Ln}^{3+}$  determination in the presence of  $\text{Sc}^{3+}$ . Preliminary investigations showed that scandium, contrary to yttrium, does not undergo extraction from  $10^{-3} \text{ mol l}^{-1}$  sodium hydroxide solution. Thus, there is possibility of determining of  $\text{Eu}^{3+}$  in the presence of  $\text{Sc}^{3+}$ . Unfortunately it was found that scandium in quantities higher than  $7 \mu\text{g}$  in 5 ml is precipitated at  $\text{pH} = 10.5$  what makes determination of  $\text{Eu}^{3+}$  in the presence of higher amounts of  $\text{Sc}^{3+}$  impossible. Hence  $\text{Eu}^{3+}$  can be determined in the solutions in which the concentration of scandium does not exceed  $7 \mu\text{g}$  in 5 ml. The determination of  $0.76 \mu\text{g}$  of  $\text{Eu}^{3+}$  in the presence of  $6.75 \mu\text{g}$  of  $\text{Sc}^{3+}$  was carried out in  $10^{-3} \text{ mol l}^{-1}$  sodium hydroxide solution using HA18C6 in the concentration of  $3 \times 10^{-5} \text{ mol l}^{-1}$ . The obtained result was  $0.72 \mu\text{g}$  of  $\text{Eu}^{3+}$  ( $n = 5$ ,  $s_r = 14\%$ ).

### Determination of $\text{Eu}^{3+}$ in the presence of aluminium

Aluminium, in the system HA18C6- $\text{E}_A$ , does not undergo extraction to a chloroform phase from  $10^{-3} \text{ mol l}^{-1}$  sodium hydroxide solution. Because of its amphoteric nature, aluminium hydroxide formed in an alkaline solution dissolves under the influence of higher concentrations of sodium hydroxide. Hence, there is possibility of preparing analyzed solutions in the medium of NaOH with  $\text{pH} = 12$ .

The use of higher concentrations of sodium hydroxide is impossible because of the need for the preservation of the optimum conditions of complexation of  $\text{Ln}^{3+}$ . It was found that 1000-fold excess of aluminium does not disturb the  $\text{Eu}^{3+}$  determination.

The example of determination was carried out for  $0.76 \mu\text{g}$  of  $\text{Eu}^{3+}$  in the presence of  $135 \mu\text{g}$  of  $\text{Al}^{3+}$  with the concentration of HA18C6 =  $3 \times 10^{-5} \text{ mol l}^{-1}$  according to the procedure described in the experimental part. Using the method of standard additions the obtained result was  $0.76 \mu\text{g}$  ( $n = 9$ ,  $s_r = 2.4\%$ ).

### Determination of $\text{Eu}^{3+}$ , $\text{Sm}^{3+}$ , $\text{Pr}^{3+}$ , $\text{Nd}^{3+}$ and $\text{Gd}^{3+}$ in the presence of gallium

Gallium, like aluminium, does not undergo extraction to chloroform phase in the medium of  $10^{-3}$  mol  $\text{l}^{-1}$  NaOH and from higher concentrated solution. Considering the fact that gallium dissolves both in acids and bases it is possible, as in the case of aluminium, to prepare analyzed solutions in sodium hydroxide of the proper concentration.

The suitability of the proposed procedure for  $\text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Gd}^{3+}$  determination was examined in the presence of 1.4 mg gallium, using HA18C6 in the concentration of  $1 \times 10^{-4}$  mol  $\text{l}^{-1}$  in the medium of  $10^{-3}$  mol  $\text{l}^{-1}$  sodium hydroxide.

The obtained results of determinations are presented in Table 3 and indicate the possibility of the determination of  $\text{Ln}^{3+}$  in gallium at the 0.02 % level.

**Table 3.** The results of determination of  $\text{Ln}^{3+}$  in a solution containing 1.4 mg of  $\text{Ga}^{3+}$  ( $n = 7$ , except for  $\text{Sm}^{3+}$   $n = 8$ )

Determined $\text{Ln}^{3+}$	Introduced $\text{Ln}^{3+}$ , $\mu\text{g}$	Found $\text{Ln}^{3+}$ $\mu\text{g}$	Standard deviation $s$	Relative standard deviation $s_r$ , %
Eu	0.38	0.38	0.072	19
Sm	0.37	0.37	0.044	12
Pr	0.35	0.32	0.035	11
Nd	0.36	0.32	0.035	11
Gd	0.39	0.39	0.066	17

### Determination of $\text{Eu}^{3+}$ , $\text{Nd}^{3+}$ , $\text{Sm}^{3+}$ , $\text{Pr}^{3+}$ , $\text{Gd}^{3+}$ and $\text{Tb}^{3+}$ in the presence of a mixture of the alkaline earth metals

Rare earth metals in the mixture with alkaline earth metals are used for the formation of mixed crystals having fluorite structure. Such systems are interesting as active media in quantum optics [11]. Thus, it is advisable to develop a procedure for the determination of rare earths in such systems.

Determination of  $\text{Ln}^{3+}$  was carried out in the medium of  $10^{-3}$  mol  $\text{l}^{-1}$  sodium hydroxide. Because in the alkaline solution  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  cations are precipitated in the form of hydroxides, in order to preserve them in the solution in the ionic form, sulphosalicylic acid in the concentration of  $1 \times 10^{-3}$  mol  $\text{l}^{-1}$  was used. Another difficulty occurring during determination of  $\text{Ln}^{3+}$  in the presence of the above mentioned cations is the ability of  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  to form complexes with HA18C6 [12], undergoing extraction to chloroform phase. This difficulty was overcome by the use of kinetic masking of these cations with  $1 \times 10^{-2}$  mol  $\text{l}^{-1}$  EDTA during the process of extraction [13].  $\text{Eu}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Tb}^{3+}$  were determined in the presence of a constant quantity of  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  amounting to 80  $\mu\text{g}$  of  $\text{Ca}^{2+}$ , 175  $\mu\text{g}$  of  $\text{Sr}^{2+}$  and 275  $\mu\text{g}$  of  $\text{Ba}^{2+}$ , using HA18C6 in the concentration of  $1 \times 10^{-4}$  mol  $\text{l}^{-1}$ . The results are presented in Table 4.

**Table 4.** The results of determinations of  $\text{Ln}^{3+}$  in solution containing 80  $\mu\text{g}$  of  $\text{Ca}^{2+}$ , 175  $\mu\text{g}$  of  $\text{Sr}^{2+}$  and 275  $\mu\text{g}$  of  $\text{Ba}^{2+}$  ( $\text{Eu}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$   $n = 8$ ,  $\text{Pr}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $n = 7$ )

Determined $\text{Ln}^{3+}$	Introduced $\text{Ln}^{3+}$ , $\mu\text{g}$	Found $\text{Ln}^{3+}$ , $\mu\text{g}$	Standard deviation $s$	Relative standard deviation $s_r$ , %
Eu	0.76	0.65	0.07	12
Nd	0.72	0.69	0.08	12
Sm	0.75	0.68	0.04	7
Pr	0.70	0.70	0.06	9
Gd	0.79	0.79	0.07	9
Tb	0.79	0.79	0.04	6

## CONCLUSIONS

The presented results allow to state that the system  $\text{Ln}^{3+}$ -HA18C6- $\text{E}_A$  can be used for the determination of  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Tb}^{3+}$  in the presence of heavy lanthanides and yttrium and also in the presence of excess of  $\text{Sc}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$  and  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ .

On the basis of the obtained results one may say that the developed procedures of determinations are characterized by good sensitivity, accuracy and precision.

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