Short communication

Separation and determination of rare earth elements by Dowex 2-X8 resin using sodium trimetaphosphate as elution agent

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Abstract

The distribution coefficients of rare earth elements and thorium with Dowex 2-X8, 200–400 mesh, a strongly basic anion-exchange resin, have been determined regarding four different concentrations of sodium trimetaphosphate ($3 \cdot 10^{-3}$, $5 \cdot 10^{-3}$, $7 \cdot 10^{-3}$ and 0.01 M). The separation of the rare earths and thorium obtained from an Australian monazite has been investigated by anion-exchange chromatography with sodium trimetaphosphate concentration gradient on a Dowex 2-X8 ion-exchange columns. The order of elution of the elements was the reverse of the order of elution of the same elements on Dowex 1 resin. The elution was investigated using 5 mg and 250 mg samples. In the separation of 5 mg samples, all elements were separated in 29 min. It has been seen that the elution peaks are narrow, tailing effects are very small, Dy and Y are well separated. Qualitative and quantitative determinations were realized by spectrofluorometry. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Rare earth ions; Thorium; Sodium trimetaphosphate

1. Introduction

As mentioned in previous work [1], the anion-exchange behaviour of many tripositive lanthanides has been investigated some authors. In addition, Surls and Choppin have been investigated this separation with ammonium thiocyanate [2]. Faris and Warton separated six rare earth elements in 19 h in nitric acid–methanol media by anion exchange [3]. Bruzzoniti et al. separated 13 rare earth elements in 25 min with concentration gradient elution of oxalic acid solutions containing diglycolic acid using ion chromatography [4].

The anion-exchange resins that were used in these studies generally had $-N(CH_3)_3^+$ functional groups

and the order of elution was from La to Lu. In the present work, resin with $-N(CH_3)_2C_2H_4OH^+$ functional groups was used. It was seen that the order of elution with this resin is from Lu to La, instead of from La to Lu. Sodium trimetaphosphate was used as a complexing eluent for the anion-exchange separation of all rare earth elements and thorium on Dowex 2-X8 resin. Sodium trimetaphosphate has some important advantages as a new elution agent over the other elution agents on Dowex 1-X4 resin [1]. In this work, the results obtained indicate that it has also same advantages on Dowex 2-X8 resin. For example, symmetrical and narrow elution curves without tailing, good separations without overlapping, shorter elution times at room temperature. It has a lower cost than other complexing agents. It is possible to recover the sodium trimetaphosphate

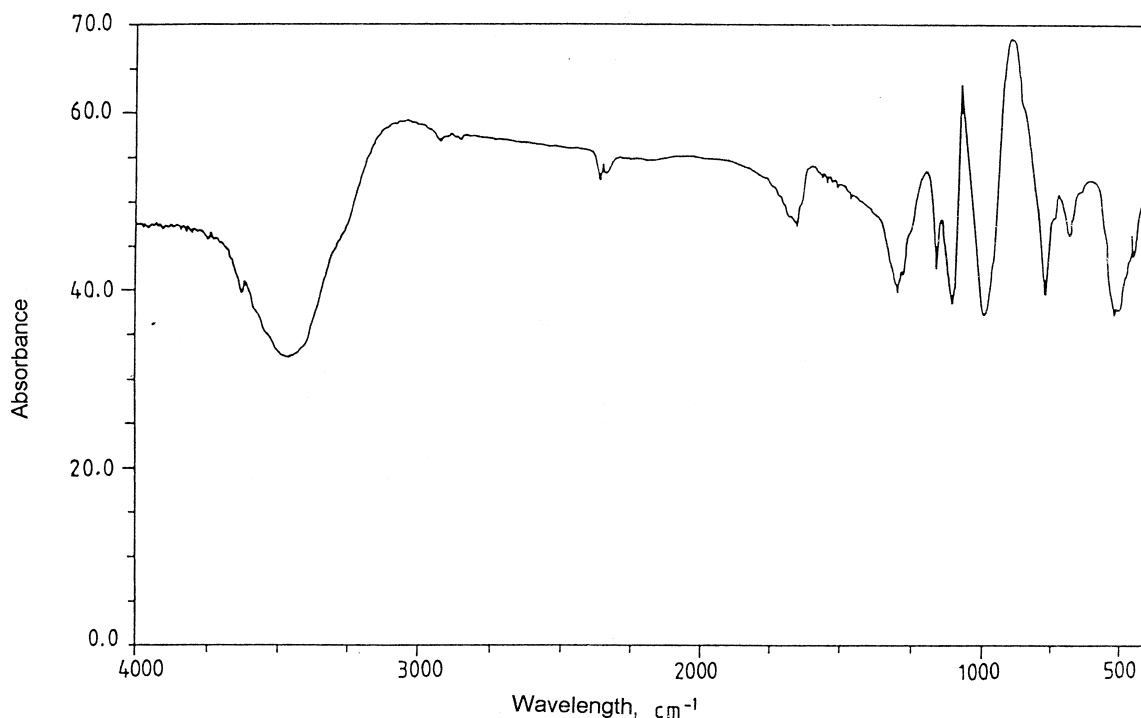*Corresponding author. Fax: +90-212-2856-386.

Fig. 1. The infrared spectrum of the $Na_3P_3O_9 \cdot 6H_2O$ (KBr disc technique).

from eluate with addition of ethanol to the solutions. In these elutions, very low concentrations of sodium trimetaphosphate were used. It was seen that these separations can be applied successfully to the different rare earth mixtures for preparative and analytical studies.

2. Experimental

2.1. Chemicals

Analytical-grade reagents of at least 99.5% pure were used. The rare earth solutions were prepared by dissolving the appropriate amount of the oxides. The oxides used were 99.9% pure. All chemicals were obtained from Fluka (Buchs, Switzerland) and Merck (Darmstadt, Germany).

The strongly basic anion exchanger Dowex 2-X8

Table 1
Anion-exchange distribution coefficients in different concentrations of sodium trimetaphosphate solutions

Rare earth elements	Concentration of sodium trimetaphosphate (M)			
	$3 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	$7 \cdot 10^{-3}$	0.01
La	190.7	120.0	75.0	6.28
Ce	165.9	113.1	66.2	5.91
Pr	147.2	97.0	60.7	5.49
Nd	132.0	94.8	58.3	5.08
Sm	116.9	89.7	55.0	4.67
Eu	91.9	60.2	45.3	4.13
Gd	74.9	49.1	36.8	3.79
Tb	65.2	42.5	30.8	3.36
Y	59.9	35.9	23.6	3.13
Dy	52.1	31.8	17.1	2.83
Ho	46.2	26.3	10.9	2.20
Er	39.7	20.3	8.22	1.80
Tm	34.9	17.2	6.85	1.50
Yb	27.3	14.5	4.71	1.15
Lu	20.9	11.6	3.09	0.99
Th	14.5	8.35	2.19	0.84

(200–400 mesh; chloride form) from Bio-Rad Labs. (Richmond, CA, USA) was used.

2.2. Equipment

The gradient elution apparatus was designed as in previous work [1].

The fluorometric measurements were made on a Perkin-Elmer 204 fluorescence spectrophotometer with a 150 W xenon arc lamp. The fluorescence intensities of solutions were measured in 10 mm quartz cells. The excitation and emission slitwidths were 10 nm.

The infrared spectrum of the prepared $Na_3P_3O_9\cdot$

$6H_2O$ has been determined with the JASCO Fourier transform infrared (FT-IR) 5300 infrared spectrophotometer using the KBr disc technique.

Two different sizes of glass columns (40×1.2 cm I.D. and 25×0.5 cm I.D.) fitted with fritted glass disks in the bottom were used.

2.3. Preparation of eluting agent and rare earth elements

Sodium trimetaphosphate solutions were prepared by dissolving $Na_3P_3O_9\cdot6H_2O$. Anhydrous sodium trimetaphosphate ($Na_3P_3O_9$) was prepared by heat-

Table 2
Fluorimetric reagents for rare earth elements and thorium

Element	Reagent	Excitation wavelength (nm)	Emission wavelength (nm)	Limit of detection ($\mu g\ ml^{-1}$)	Ref.
La	8-Hydroxy-quinoline-5-sulphonic acid	365	530	1–20	[10]
Ce	0.1 M sodium trimetaphosphate	297	340	10^{-3}–75	[11]
Pr	H_3PO_4	217	275	4	[12]
Sm	0.015 M oxalic acid	259	644	0.8	[13]
Eu	1.5 M K_2CO_3	400	620	4–800	[14]
Gd	0.5 M Na salicylate, Rhodamine S	546	571	3–30	[15]
Tb	0.01 M potassium oxalate	255	545	$5\cdot10^{-2}$–10	[16]
Dy	$3\cdot10^{-4}$ M acetyl acetone in 95% ethanol	310	581	0.054–0.482	[17]
Tm	0.01 M nalidixic acid, 40% hexamine	450	510	200	[18]
Lu	Morin, diantipyrylmethane, ClO_4^-	425	508	0.02	[19]
Y	0.5% 8-hydroxy-quinoline solution in 1 M HOAc	430	510	10–50	[20]
Th	Morin	410	520	0.88	[21]

ing sodium hexametaphosphate for 8–12 h at 500°C [5]. The 6-hydrate, $Na_3P_3O_9 \cdot 6H_2O$, was prepared from anhydrous salt [6]. The infrared spectrum of the prepared $Na_3P_3O_9 \cdot 6H_2O$ has been determined using the KBr disc technique (Fig. 1). It was seen that this spectrum is similar to the original spectrum given in the literature [7].

Rare earth elements were separated from an Australian monazite concentrate as the mixture of their oxides by conventional benzoic acid method [8]. But, Th was not separated from rare earths by precipitation. Because, as can be seen from distribution coefficients, it is possible to separate all rare earth elements and thorium with anion-exchange elution in sodium trimetaphosphate media on Dowex 2-X8 resin.

3. Procedure

3.1. Distribution coefficients

The resin was conditioned to the chloride form by passing 2 *M* HCl, 2 *M* NaOH and 2 *M* HCl, respectively through the resin column and each time the resin was washed by passing distilled water, finally it was dried in air.

The determination of distribution coefficients was determined using 0.5 g of dry resin (its mass corrected as the oven dried resin at 105°C).The resin was equilibrated in a small column with sodium trimetaphosphate solution in the desired concentration until equilibration. It was transferred to a glass stoppered flask. Then, 50 ml of eluent at known
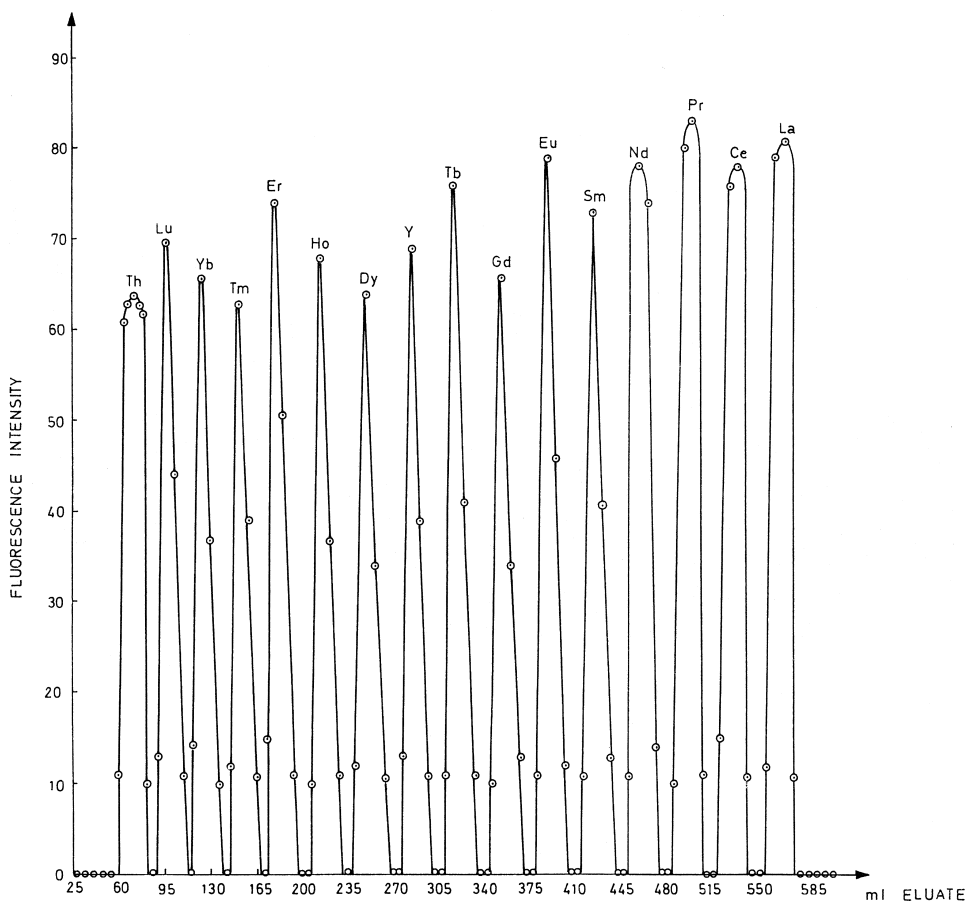

Fig. 2. Elution curves of the elements (in 250 mg of rare earth oxides obtained from monazite) with first 193 ml $7 \cdot 10^{-3}$ *M* and then a $7 \cdot 10^{-3}$–0.01 *M* concentration gradient of sodium trimetaphosphate; resin bed 1.2 cm diameter; 36 cm length; flow-rate 2 ml min^{-1}.

concentration and containing 1 mequiv. of the cation was added. The flask was shaken for 15 h with a mechanical shaker at room temperature.

The fluorescence intensities of solutions were measured before and after equilibrium. The distribution coefficients K_d were calculated by the following equation:

$$K_d = \frac{I_0 - I}{I} \times \frac{\text{ml of solution}}{\text{g of dry resin}}$$

where I_0 and I are the fluorescence intensities of the solution before and after equilibration with the resin.

The coefficients are presented in Table 1.

3.2. Elutions

The strongly basic anion-exchange resin Dowex 2-X8 was washed several times with distilled water to remove the fine particles. The washed resin was transferred to the column in a water slurry after it was kept in water overnight. Subsequently it was equilibrated by passing the elution solution through the column. Then the sample solution was added to the top of the resin column. The adsorbed sample in the upper part of the resin column was eluted. Convenient volumes of fractions were collected with an automatic fraction collector.
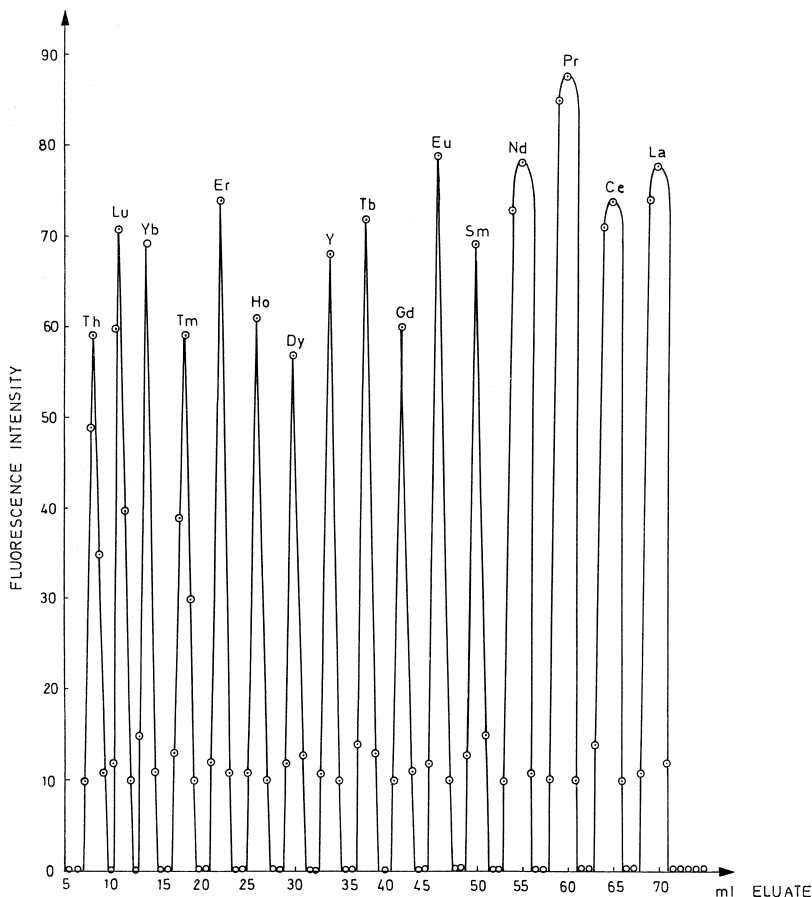

Fig. 3. Elution curves of the elements (in 5 mg of rare earth oxides obtained from monazite) with first, 23 ml $7 \cdot 10^{-3}$ M and then a $7 \cdot 10^{-3}$–0.01 M concentration gradient of sodium trimetaphosphate; resin bed 0.5 cm diameter, 23 cm length; flow-rate 2 ml min^{-1}.

3.3. Identification

The elements in the eluted fractions were defined by spectrofluorometry using morin [9]. The qualitative identification of individual rare earth elements were realized using appropriate fluorometric reagents Table 2. Since the appropriate fluorometric reagent was not found for Nd, Ho, Er and Yb, they were precipitated from the eluate with oxalic acid. The rare earth oxides were obtained by ignition of these oxalate precipitates and the elements were identified from the colour of their oxides. The quantitative determination of each element in the fractions were also realized with appropriate fluorimetric reagent using calibration curves.

4. Results and discussion

A 250-mg amount of the mixture of rare earth oxides was obtained from the Australian monazite. It was dissolved in dilute HNO_3 by heating. Cerium was reduced with H_2O_2. The solution was then evaporated almost to dryness. Afterwards it was reevaporated twice in the same manner following the addition of 0.5 ml concentrated HCl. The sample was dissolved in 3 ml $3 \cdot 10^{-3}$ M sodium trimetaphosphate solution and it was transferred to the column containing a resin bed 36 cm in length which was pre-equilibrated with 250 ml of $7 \cdot 10^{-3}$ M sodium trimetaphosphate solution. The top of the column was previously rinsed with a small amount of water.
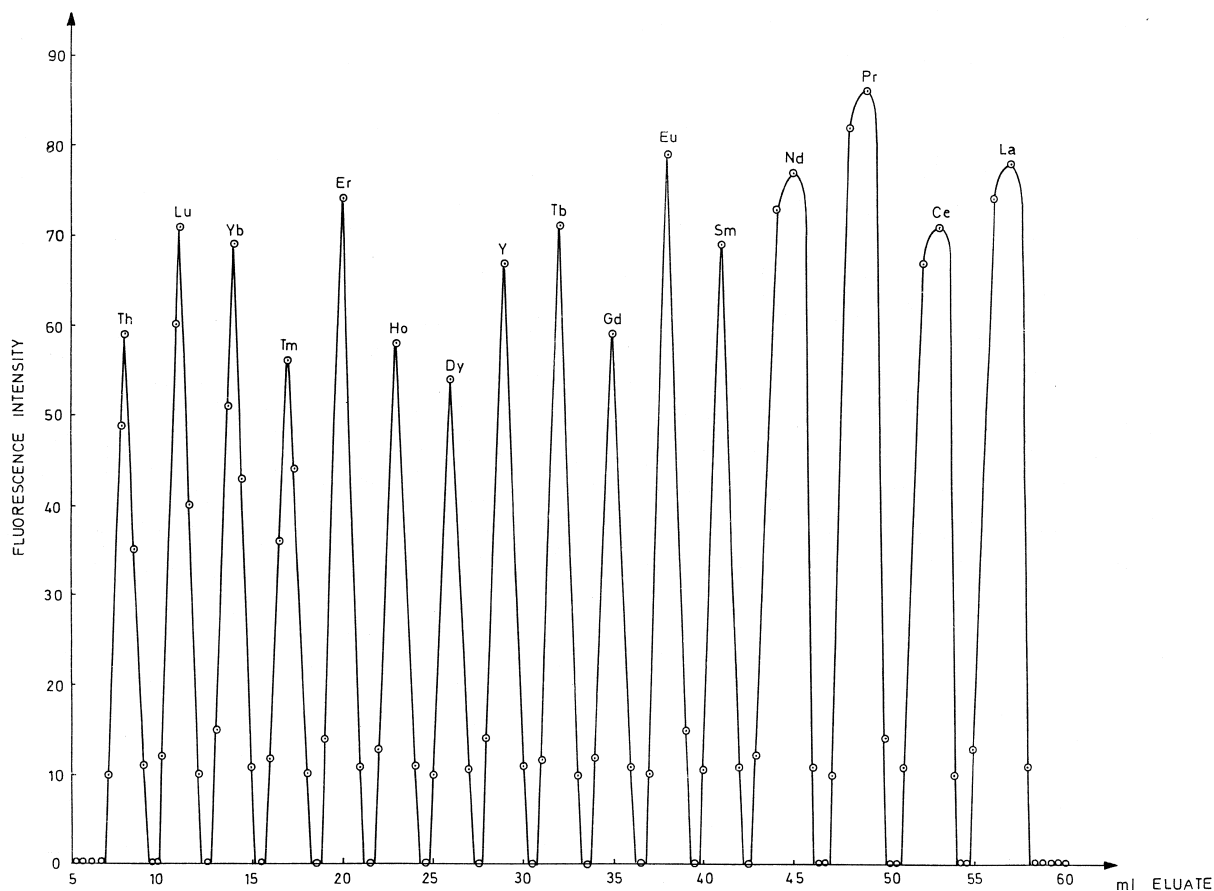

Fig. 4. Elution curves of the elements (in 5 mg of rare earth oxides obtained from monazite) with first 15 ml $7 \cdot 10^{-3}$ M and then a $7 \cdot 10^{-3}$–0.01 M concentration gradient of sodium trimetaphosphate; resin bed 0.5 cm diameter, 23 cm length; flow-rate 2 ml min^{-1}.

The results obtained from distribution coefficients were examined. In the first part of elution, a $7 \cdot 10^{-3}$ M sodium trimetaphosphate solution was used. After 193 ml effluent was taken, the elution was performed using a concentration gradient of $7 \cdot 10^{-3}$–0.01 M sodium trimetaphosphate. A flow-rate of 2 ml min^{-1} was used. The elution curves are shown in Fig. 2. All the rare earth elements and thorium were separated completely from each other. Two hundred and fifty mg is a preparative amount and it is possible to obtain preparatively the rare earth elements with high percentage in the monazite.

On the other hand, this elution procedure was applied to a 5 mg amount of the mixture of rare earth oxides prepared from the Australian monazite. The 5-mg amount of the mixture of rare earth oxides was dissolved and prepared as described above. The sample solution was transferred to the top of the small column containing a resin bed 23 cm in length which was pre-equilibrated with 250 ml of $7 \cdot 10^{-3}$ M sodium trimetaphosphate solution. In the first part of this elution, $7 \cdot 10^{-3}$ M sodium trimetaphosphate was used. After 23 ml effluent was taken, concentration gradient of $7 \cdot 10^{-3}$–0.01 M sodium trimetaphosphate was applied. The elution curves are indicated in Fig. 3. In order to obtain shorter separation time, another elution was carried out with the same amount of the sample. After 15 ml $7 \cdot 10^{-3}$ M sodium trimetaphosphate was taken, elution was performed using concentration gradient of $7 \cdot 10^{-3}$–0.01 M sodium trimetaphosphate. A flow-rate of 2 ml min^{-1} was used. The separations were very well and there was no overlapping. The elution curves are shown in Fig. 4. Separations were completed in 29 min. The order of elution of the elements was the reverse of the order of elution of the same elements on Dowex 1 resin [1]. For quantitative determination, the fraction of each element was collected in a volumetric flask and the amounts of the elements were determined fluorimetrically preparing the calibration graph with morin reagent.

5. Conclusion

In this study, Dowex 2-X8 resin with $-N(CH_3)_2CH_2CH_2OH^+$ functional groups was used.

It was shown that the order of elution is from Lu to La the reverse of the elution order of Dowex 1-X4 resin. Furthermore, it has been demonstrated that sodium trimetaphosphate is a very suitable new elution agent for the separation of rare earths and thorium on strongly basic anion-exchange resin Dowex 2-X8 at room temperature. By using a concentration gradient of elution very good separations were obtained.

It was seen that these separations can be applied successfully to different rare earth mixtures for preparative and analytical studies.

References

[1] Ş. Kutun, A. Akseli, J. Chromatogr. A 847 (1999) 261.
[2] J.P. Surls, G.R. Choppin, J. Inorg. Nucl. Chem. 4 (1957) 62.
[3] J.P. Faris, J.W. Warton, Anal. Chem. 34 (9) (1962) 1077.
[4] M.C. Bruzzoniti, E. Mentasti, C. Sarzanini, M. Braglia, G. Cocito, J. Kraus, Anal. Chim. Acta 322 (1996) 49.
[5] S. Budavari, in: The Merck Index, 11th Edition, Merck, Rahway, NJ, 1989, p. 1370.
[6] L.F. Audrieth, in: Inorganic Synthesis, Vol. 3, McGraw-Hill, New York, 1950, p. 104.
[7] S. Greenfield, M. Clift, in: Analytical Chemistry of the Condensed Phosphates, Pergamon Press, 1975, p. 137.
[8] I.M. Kolthoff, P. Elving, in: 8th Edition, Treatise on Analytical Chemistry, Part II, Vol. 8, Interscience, New York, 1963, p. 22.
[9] C.T. Huu, A.I. Volkova, T.E. Get'man, Ser. Khim. 12 (1971) 43.
[10] S.B. Meshkova, N.V. Rusakova, N.S. Poluektov, Zh. Anal. Khim. 37 (11) (1982) 1988.
[11] Y. Rakicioğlu, A. Akseli, J. Florescence 8 (1) (1998) 45.
[12] W. Liu, Fenxi Huaxue 17 (4) (1989) 362.
[13] H. Huang, X. Gao, Y. Hu, Bunseki Kagaku 39 (4) (1990) 233.
[14] T. Taketatsu, M.A. Carey, C.V. Banks, Talanta 13 (1966) 1081.
[15] A.T. Pilipenko, D.I. Bakardzhieva, A.I. Volkova, T.E. Get'man, Ukr. Khim. Zh. 37 (7) (1971) 689.
[16] G. Alberti, M.A. Massucci, Anal. Chim. Acta 35 (1966) 303.
[17] M. Elbanowski, S. Lis, Fresenius Z. Anal. Chem. 332 (1988) 63.
[18] A.V. Egorova, S.V. Bel'tyukova, N.S. Poluektov, Ukr. Khim. Zh. 53 (2) (1987) 184.
[19] N.S. Poluektov, R.S. Laver, O.F. Gaidarzki, Zh. Analit. Khim. 26 (5) (1971) 898.
[20] M. Ishibashi, T. Shigematsu, Y. Nishikawa, Nippon Kagaku Zasshi 77 (1956) 1474.
[21] R.G. Milkey, M.H. Fletcher, J. Am. Chem. Soc. 79 (1957) 5425.