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Distribution Coefficients and Cation-Exchange Separation of Rare Earths in Sodium Trimetaphosphate Media and Application to Monazite

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ABSTRACT

Sodium trimetaphosphate was investigated as a new complexing agent for the cation-exchange separation of rare earths. Cation-exchange equilibrium distribution coefficients with Dowex 50 W-X8, 200–400 mesh, a sulfonated polystyrene resin, are presented for 15 rare earth elements and thorium in different concentration ranges between 0.01 and 0.3 M sodium trimetaphosphate. The distribution coefficients were determined at a total amount of cation to total resin capacity ratio $q = 0.4$. By considering these distribution coefficients, a good separation of all lanthanides were achieved by using concentration gradient elution with sodium trimetaphosphate at room temperature. Sodium trimetaphosphate has the following advantages over α-hydroxyisobutyrate as an eluting agent: The elution peaks are narrow and nearly symmetrical, the tailing effects are very small and there is no overlapping, the separation time is shorter, and the eluent concentration is smaller than those of other known methods. Dy and Y are well separated. This separation has been successfully applied to different rare earth mixtures for determination, purification, and preparative purposes. For example, it was applied to the 5 and 250 mg rare earth oxides obtained from monazite. All rare earths and thorium were separated in 23.5 minutes in small-scale separation by concentration gradient elution with sodium trimetaphosphate. Qualitative and quantitative determinations of eluted ions were performed by spectrofluorimetry.

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INTRODUCTION

Because of their similar chemical and physical properties, it is difficult to separate and determine individual rare earth elements in their mixtures.

Some papers about the separations of the rare earth elements by ion-exchange methods were published in the *Journal of the American Chemical* Society in 1947. Since then, different complexing agents have been investigated as eluants, e.g., lactates, citrates, aminopolyacetic acids, and α-hydroxyisobutyrate (α-HIBA). It was found that α-HIBA is the best among these. A number of publications have reported using α-HIBA as an eluant. Initially, separation times were very long. For example, Zeligman separated 10 rare earth elements obtained from fission products in about 32 hours (1). Attempts have been made to reduce the separation times during subsequent years. Wish and Foti separated eight rare earth elements in 5.5 hours with pH gradient elution (2). Campbell separated 14 lanthanides in 1 to 2 hours with pressurized ion-exchange chromatography, but there were some overlapping (3). Using high-pressure liquid chromatographic (HPLC) separations with α-HIBA, Elchuk and Cassidy achieved a separation time of less than 20 minutes for microgram amounts of lanthanides (4). Barkley et al. completed the separation of nanogram amounts of rare earths in 16 minutes (5). Tielrooy et al. separated microgram amounts of lanthanides in more than 24 minutes (6). In all of these studies there was some overlapping; Dy and Y always overlapped. On the other hand, HPLC methods require expensive equipment.

Sodium trimetaphosphate was investigated in this study as a new complexing agent for the cation-exchange separation of the rare earth elements. Its separation factors are a little smaller than those of α-HIBA. However, it has the following advantages over α-HIBA as an eluant. It is possible to obtain good separation of all rare earth elements and thorium by using only concentration gradient elution without any pH change. The elution peaks are narrow and nearly symmetrical compared to those of the other eluants. The tailing effects are very small, and there is no overlapping between adjacent peaks.

Good separation of yttrium from dysprosium is especially important because they are always overlapped in other known ion-exchange separations of rare earth elements, even on a nanogram scale.

Sodium trimetaphosphate has a lower cost than other complexing agents, and elution can be performed at room temperature. The eluant concentration required is smaller than for other eluants. It is convenient for the determination, preparative separation, and purification of all the rare earth elements in their different mixtures. Another advantages is that sodium trimetaphosphate can be recovered from the eluate by adding ethyl alcohol to the solution.

In this study, using relatively simple equipment, a separation time of 23.5 minutes was achieved for elements which were in a 5-mg mixture of rare earths and thorium oxides obtained from monazite. Compared to similar work using different eluting agents, this result is extremely satisfactory. It is similar or better than the best results of HPLC separations.

EXPERIMENTAL

Chemicals

The rare earths solutions were prepared by dissolving their oxides. The oxides used were 99.9% pure. Other chemicals were of analytical-reagent grade and at least 99.5% pure. All chemicals were obtained from Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland). The strongly acidic cation exchange resin Dowex 50 W-X8, 200–400 mesh, marketed by Bio-Rad Laboratories (Richmond, CA, USA) was used. Distilled water was used to prepare the solutions.

Equipment

The gradient elution apparatus consisted of two flasks. Eluting solution (500 mL) of a convenient concentration was placed in each flask. A second flask was equipped with a magnetic stirrer. The two flasks were connected by a tube with three-way tap and a bulb. In order to adjust the flow rate, a peristaltic pump was placed between the second flask and the resin column. Two different sized glass columns (1.2 cm i.d., 40 cm length; 0.5 cm i.d., 25 cm length) fitted with a fritted glass disk in the bottom were used. Fractions were collected with an automatic fraction collector.

The fluorometric measurements were carried out on a Perkin-Elmer 204 Fluorescence Spectrophotometer (Norwalk, CT, USA) 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.

Preparation of Eluting Agent and Rare Earth Elements

Sodium trimetaphosphate was used as the eluting agent. Anhydrous sodium trimetaphosphate was prepared from sodium hexametaphosphate (7), and then $Na_3P_3O_9 \cdot 6H_2O$ was prepared from its anhydrous salt (8).

The rare earth elements were separated from an Australian monazite concentrate as a mixture of their oxides by the conventional benzoic acid method (9). The results of this analysis are given in Table 1.

TABLE 1
Analysis of the Australian Monazite

Insoluble (%)	ThO_2 (%)	Rare earth oxides (%)
2.93	8.38	56

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PROCEDURE

Distribution Coefficients

The resin was conditioned to the hydrogen form by passing 2 M HCl, 2 M NaCl, and 2 M HCl individually through the resin column, and each time the resin was washed by passing distilled water, finally, it was dried in air.

TABLE 2
Fluorimetric Reagents for Rare Earth Elements and Thorium

Element	Reagent	Excitation wavelength (nm)	Emission wavelength (nm)	Limit of detection μg·mL^{-1})	Reference
La	8-Hydroxy-quinoline-5-sulfhonic acid	365	530	1–20	11
Ce	0.1 M sodium trimeta-phosphate	297	340	10^{-3}–75	12
Pr	H_3PO_4	217	275	4	13
Sm	0.015 M oxalic acid	259	644	0.8	14
Eu	1.5 M K_2CO_3	400	620	4–800	15
Gd	0.5 M Na salicylate, Rhodamine S	546	571	3–30	16
Tb	0.01 M potassium oxalate	255	545	5×10^{-2}–10	17
Dy	3×10^{-4} M acetylacetone in 95% ethanol	310	581	0.054–0.482	18
Tm	0.01 M nalidixic acid in 40% hexamine	450	510	200	19
Lu	Morin, diantipyrinyl-methane, $C1O_4^-$	425	508	0.02	20
Y	0.5% 8-hydroxy-quinoline solution in 1 N HOAc	430	510	10–50	21
Th	Morin	410	520	0.88	22

A portion (0.5 g) of resin, conditioned to the hydrogen form and its mass corrected as the oven-dried resin at 105°C was transferred into a glass-stoppered flask. Then 50 mL of eluant of a known concentration and containing 1 meq of the cation was added. The flask was shaken in a mechanical shaking device for 15 hours at room temperature.

Fluorescence measurements with appropriate reagents were carried out before and after equilibrium in the solution. The fluorimetric reagents used for each element are shown in Table 2. The distribution coefficient K_d is defined by

$$K_\mathrm{d} = \frac{I_0 - I}{I} \times \frac{\text{mL of solution}}{\text{g of dry resin}}$$

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

Identification

The elements in the fractions of eluate were defined by spectrofluorometry using morin (10). The qualitative identification of individual rare earth elements was realized by using appropriate fluorometric reagents as shown in Table 2. Nd, Ho, Er, and Yb were precipitated from the eluate with oxalic acid because fluorimetric reagents were not found for them. The rare earth oxides were obtained by ignition of these oxalate precipitates, and the elements were identified from the color of their oxides.

For quantitative determination, fractions of each element were collected in a volumetric flask and the amounts of the elements were determined fluorimetrically by preparing calibration graphs with the appropriate reagent. The results are shown in Table 3.

TABLE 3
Quantitative Analysis Results of Rare Earth Elements in Australian Monazite

Element	%	Element	%
La	18.76	Y	0.76
Ce	40.38	Dy	0.08
Pr	7.59	Ho	0.08
Nd	15.32	Er	0.08
Sm	7.60	Tm	0.08
Eu	0.08	Yb	0.76
Gd	2.99	Lu	0.76
Tb	0.76		

Elutions

Dowex 50 W-X8, 200–400 mesh resin was washed several times with distilled water; each time the fine particles were decanted off. The washed resin was kept in water overnight and then transferred to the column in a water slurry. It was subsequently equilibrated by passing an eluting solution through the column. The sample solution was then added to the top of the resin column which had been previously rinsed with a small amount of water. The adsorbed sample in the upper part of the resin column was eluted. Fractions of a convenient volume were taken for fluorimetric measurements.

RESULTS AND DISCUSSIONS

Systematically compiled data on ion-exchange equilibrium distribution coefficients are very useful for planning separations. Therefore, the distribution coefficients were determined and are presented in Table 4. As can be seen from this table, the distribution coefficients decrease with increasing sodium trimetaphosphate concentration and atomic number of the lanthanides. Yttrium is located between terbium and dysprosium, and thorium is placed before lutetium.

TABLE 4
Cation Exchange Distribution Coefficients in Different Concentrations of Sodium Trimetaphosphate Solutions

Rare earth elements	Molarity of sodium trimetaphosphate			
	0.01 M	0.05 M	0.1 M	0.3 M
La	1704	182	78	6.3
Ce	1341	167	61	5.9
Pr	1138	166	58	5.4
Nd	1008	165	53	4.9
Sm	825	163	52	4.8
Eu	543	155	40	4.3
Gd	346	121	38.1	4.28
Tb	208	118	37.6	4.21
Y	198	107	19.5	4.17
Dy	196	103	18.8	4.14
Ho	174	96	17	3.9
Er	159	86	14	3.5
Tm	129	74	13	3.1
Yb	107	66	10	3
Lu	97	59	9.5	2.96
Th	76	36	8	1.5

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The following separations were performed by considering these distribution coefficient values.

Separation of Lanthanides in a Synthetic Mixture

An approximately 3.5 mL solution of a synthetic mixture which contained 0.05 meq of each lanthanide element was prepared. The sample as an aqueous solution was added to a column containing a resin bed 36 cm in length which had been previously equilibrated by passing about 250 mL of 0.3 M sodium trimetaphosphate solution through it. Lanthanides were subsequently eluted using a concentration gradient of 0.05–0.3 M sodium trimetaphosphate at a flow rate of 0.5 mL·min^{-1}. Fractions of 7 mL volume were taken using an automatic fraction collector. Lanthanides in the fractions were defined fluorimetrically with morin. The elution curves are shown in Fig. 1. As can be seen,

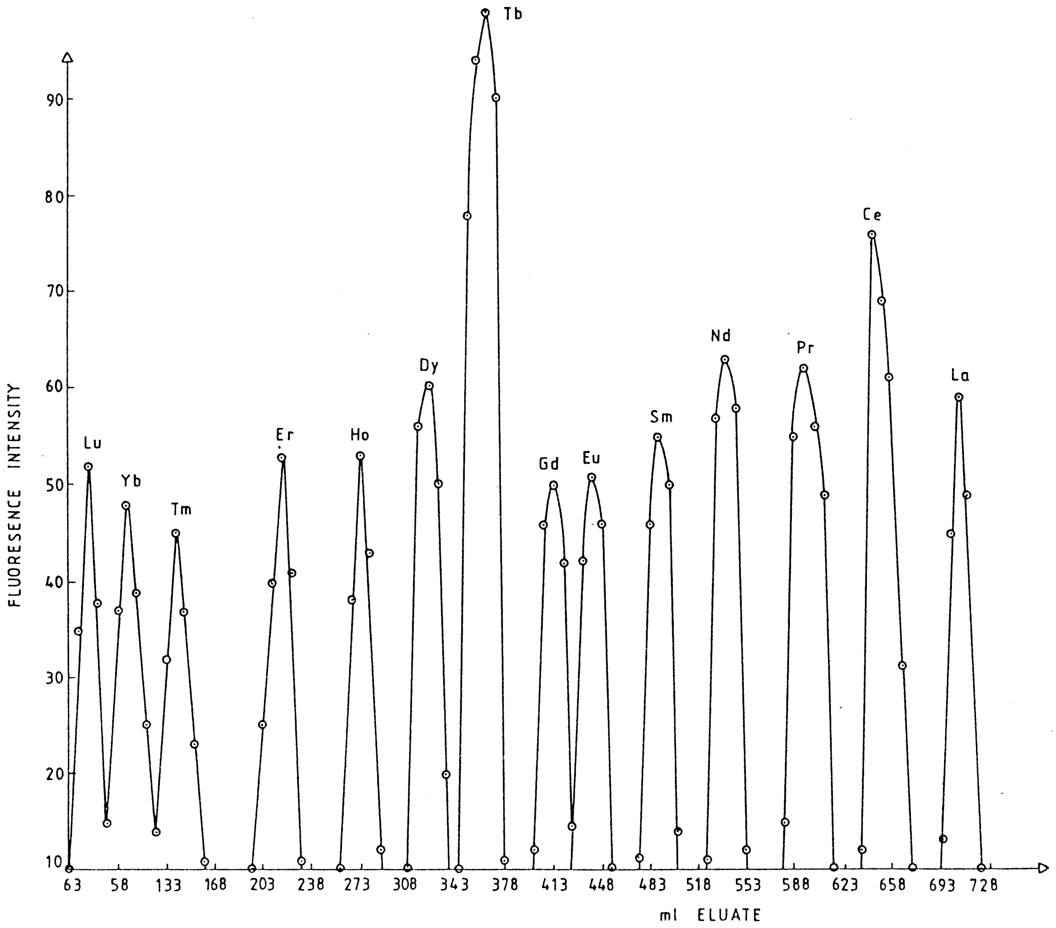

FIG. 1 Elution curves of 14 lanthanides (0.05 meq of each) with a 0.05–0.3 M concentration gradient of sodium trimetaphosphate; resin bed 1.2 cm diameter, 36 cm length; flow rate 0.5 mL·min^{-1}.

all lanthanides were separated from each other and there was only a little overlapping in Lu-Yb-Tm. The elution curves are narrow and the tailing effect is very small. One the other hand, it was seen that it is possible to precipitate and recover sodium trimetaphosphate by adding ethyl alcohol to the eluate. By adding saturated oxalic acid to the filtrate, it is possible to precipitate the rare earth oxalates. Ignition of these oxalates yields the oxide of each element. Therefore, this method can be use for the purification of rare earths.

It appeared possible to apply this elution procedure to a monazite sample in order to recover the rare earth elements from monazite.

Separation of Rare Earth Elements Obtained from Monazite

In the first part of the study, 250 mg of a mixture of rare earth oxides was prepared from Australian monazite as described above. It was dissolved in di-

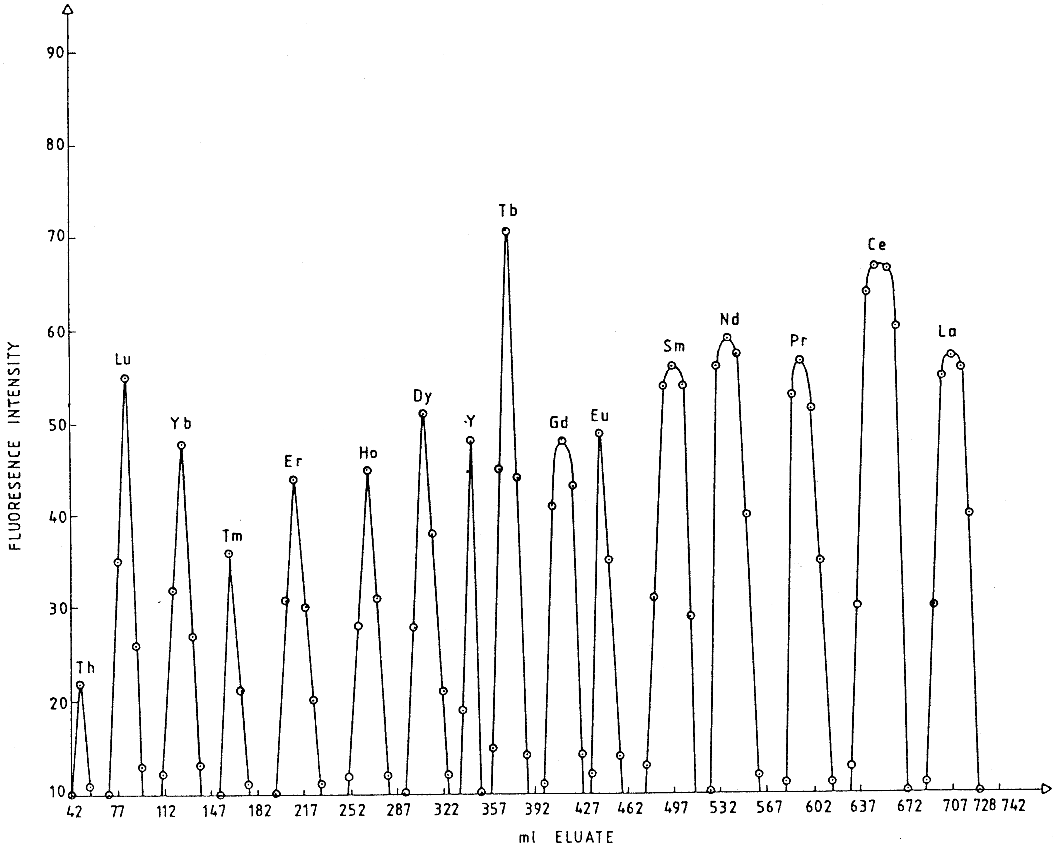

FIG. 2 Elution curves of the elements (in 250 mg of the rare earth oxides obtained from monazite) with a 0.05–0.3 M concentration gradient of sodium trimetaphosphate, resin bed 1.2 cm diameter, 36 cm length; flow rate 0.5 mL·min^{-1}.

lute HNO_3 by heating. Cerium was then reduced with H_2O_2 by evaporating the obtained solution almost to dryness. Afterward it was reevaporated twice, following the addition of 0.5 mL HCl. The sample was transferred as an aqueous solution to the top of the equilibrated resin column which had been previously rinsed with a small amount of water. Elution was performed by using a concentration gradient of 0.05–0.3 M sodium trimetaphosphate at a flow rate of 0.5 mL·min^{-1}. The elution curves are shown in Fig. 2. All the rare earth elements and yttrium were eluted within 728 mL of effluent and were separated completely from each other. The residual thorium in the mixture was eluted

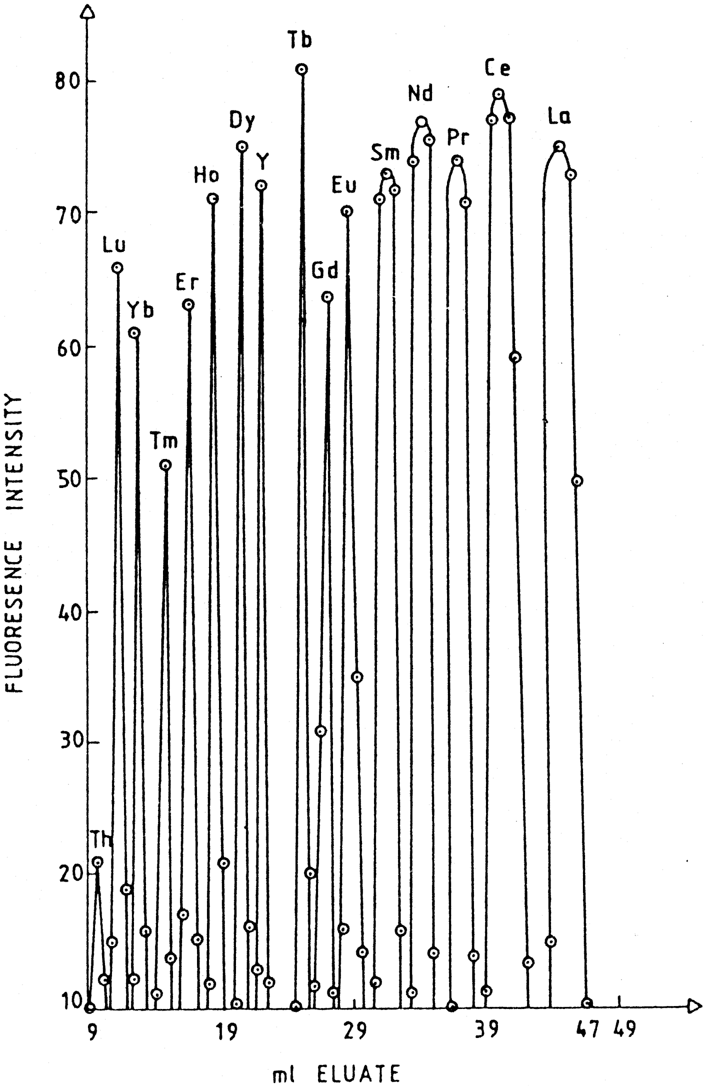

FIG. 3 Elution curves of the elements (in 5 mg of the rare earth oxides obtained from monazite) with 0.3–0.1 M concentration gradient of sodium trimetaphosphate; resin bed 0.5 cm diameter, 23 cm length; flow rate 2 mL·min^{-1}.

before lutetium. There was no overlapping, which is especially important for yttrium because in the elution procedures of rare earths with α-HIBA, yttrium overlaps with dysprosium even in nanogram scale separations. It is possible to obtain the rare earth elements preparatively with a high percentage in monazite with a 250-mg sample.

In the second part of this study, 5 mg of the mixture of rare earth oxides prepared from monazite was taken. Its solution was prepared as described above and transferred to the top of a small column containing a resin bed 23 cm in length which had been previously equilibrated with 250 mL of 0.1 M sodium trimetaphosphate. The adsorbed sample in the upper part of the resin column was eluted by using a concentration gradient of 0.3–0.1 M sodium trimetaphosphate at a flow rate of 2 $\mathrm{mL \cdot min^{-1}}$. As can be seen from Fig. 3, elution was completed in 23.5 minutes. The separations were very good and there was no overlapping. Yttrium was well separated from dysprosium.

CONCLUSION

Sodium trimetaphosphate is a very suitable new eluting agent for the separation of rare earths and thorium at room temperature. It has some advantages over other eluting agents and α-HIBA. Its eluant concentration is smaller than for other eluants. The elution peaks are narrow and nearly symmetrical. The tailing effects are very small and there is no overlapping. Dy and Y are well separated. It is possible to recover sodium trimetaphosphate. The separation time is shorter than those of other known methods. This method is convenient for the determination, preparative separation, and purification of rare earths.

REFERENCES

1. M. M. Zeligman, *Anal. Chem.*, *37*, 524 (1965).
2. L. Wish and S. C. Foti, *J. Chromatog.*, *20*, 585 (1965).
3. D. O. Campbell, *J. Inorg. Nucl. Chem.*, *35*, 3911 (1973).
4. S. Elchuk and R. M. Cassidy, *Anal. Chem.*, *51*, 1434 (1979).
5. D. J. Barkley, M. Blanchette, R. M. Cassidy, and S. Elchuk, *Ibid.*, *58*, 2222 (1986).
6. J. A. Tielrooy, P. H. M. Vleeschhouwer, J. C. Kraak, and F. J. M. Maessen, *Anal. Chim. Acta*, *207*, 149 (1988).
7. S. Budavari, *The Merck Index*, 11th ed., Rahway, NJ, 1989, p. 1370.
8. L. F. Audrieth, *Inorganic Synthesis*, *Vol. 3*, McGraw-Hill, New York, NY 1950, p. 104.
9. C. T. Huu, A. I. Volkova, and T. E. Get’man, *Ser. Khim.*, *12*, 43 (1971).
10. I. M. Kolthoff and P. Elving, *Treatise on Analytical Chemistry*, *Part II, Vol. 8*, Wiley-Interscience, New York, NY, 1963.
11. S. B. Meshkova, N. V. Rusakova, and N. S. Poluektov, *Zh. Anal. Khim.*, *37*(11), 1988 (1982).
12. Y. Rakicioğlu and A. Akseli, *J. Fluorescence*, *8*(1), 45 (1998).
13. W. Liu, *Fenxi Huaxue*, *17*(4), 362 (1989).
14. H. Huang, X. Gao, and Y. Hu, *Bunseki Kagaku*, *39*(4), 233 (1990).

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270 Madison Avenue, New York, New York 10016

15. T. Taketatsu, M. A. Carey, and C. V. Banks, *Talanta*, *13*, 1081 (1966).
16. A. T. Pilipenko, D. I. Bakardzhieva, A. I. Volkova, and T. E. Get'man, *Ukr*. *Khim*. *Zh*., *37*(7), 689 (1971).
17. G. Alberti and M. A. Massucci, *Anal*. *Chim*. *Acta*, *35*, 303 (1966).
18. M. Elbanowski and S. Lis, *Fresenius Z*. *Anal*. *Chem*., *332* 63 (1988).
19. A. V. Egorova, S. V. Bel'tyukova, and N. S. Poluektov, *Ukr*. *Khim*. *Zh*., *53*(2), 184 (1987).
20. N. S. Poluektov, R. S. Laver, and O. F. Gaidarzki, *Zh*. *Anal*. *Khim*., *26*(5), 898 (1971).
21. M. Ishibashi, T. Shigematsu, and Y. Nishikawa, *Nippon Kagaku Zasshi*, *77*, 1474 (1956).
22. R. G. Milkey and M. H. Fletcher, *J*. *Am*. *Chem*. *Soc*., *79*, 5425 (1957).

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