

# New Fluorimetric Reagents, Sodium Pyrophosphate, Sodium Trimetaphosphate, and Sodium Tetrametaphosphate, for the Determination of Cerium(III)

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Three sensitive and selective new alternatives for fluorometric determination of cerium(III) are described in this study. Ce(III) is highly fluorescent in sodium pyrophosphate, sodium trimetaphosphate, and sodium tetrametaphosphate solutions. For these reagents, the maximum excitation/emission wavelengths are 300/350, 297/340, and 299/352 nm, respectively. Maximum fluorescence intensities are obtained by irradiating Ce(III) dissolved in 0.033 g L<sup>-1</sup> sodium pyrophosphate, 41.4 g L<sup>-1</sup> sodium trimetaphosphate, and 0.96 g L<sup>-1</sup> sodium tetrametaphosphate at room temperature. The fluorescence intensities are linear over the range 0.001–30, 0.001–75, and 0.001–70 µg ml<sup>-1</sup>. The detection limits are calculated as  $9.5 \times 10^{-3}$ ,  $1.1/10^{-3}$ , and  $3.8 \times 10^{-3}$  µg ml<sup>-1</sup> Ce(III), respectively. The relative standard deviations for 15/0.05 µg ml<sup>-1</sup> Ce(III) are 1.1/1.2, 1/1.1, and 1.2/1.3%, respectively. Quenching effects of other lanthanides and some inorganic anions were investigated. The methods have been applied to rare earth mixtures with a good accuracy.

**KEY WORDS:** Cerium determination; fluorimetry; sodium pyrophosphate; sodium trimetaphosphate; sodium tetrametaphosphate.

## INTRODUCTION

It is difficult to determine individual lanthanides from their mixtures since they have very similar chemical properties.

Analytically, cerium is usually differentiated from its lanthanide family members on the basis of the strong oxidizing power of cerium(IV) in acidic solution. The addition of small amounts of cerium to steel significantly modified its properties. Therefore, the accurate determination of cerium at trace levels is very important industrially. Several absorption photometric methods are based on the ability of cerium(IV) to oxidize organic reagents to colored products. Since fluorimetric methods are inherently more sensitive and selective than absorp-

tion methods, it was considered worthwhile to develop fluorimetric procedures for the determination of trace amounts of this increasingly important element.

Fluorimetric determinations of trace amounts of cerium has been accomplished by several workers [1–36]. But these methods present difficulties, especially when the analyses are made in the region below parts per million of cerium.

Most of these methods are based on the fluorescence of cerium(III) in dilute sulfate and chloride solutions at different pH levels [1–17], but several interfering species (e.g., Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup>) exist in acidic media. A fluorimetric determination of cerium by means of sulfonaphtholazoresorcinol has been reported by Hjeu *et al.* [22]. A fluorimetric method for the determination of cerium(IV) has been based on the oxidation of oxine-5-sulfonic acid in sulfuric acid medium [25]. Navas *et al.* have reported that the reagent sodium 4,8-diamino-1,5-

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Table I. Summary of Several of the Best Methods for the Fluorimetric Determination of Cerium

Reagent	Limit of detection ( $\mu\text{g ml}^{-1}$ )	Linear range ( $\mu\text{g ml}^{-1}$ )	Ref.
H <sub>2</sub> SO <sub>4</sub>	—	$1.0 \times 10^{-3}$ – $1.0 \times 10^{-1}$	8
HCl	—	$1.4 \times 10^{-2}$ – $1.4 \times 10^{-1}$	13
Sulfonaphtholazoresorcinol	$5.0 \times 10^{-2}$	—	22
Oxine-5-sulfonic acid	—	$1.0 \times 10^{-2}$ –3.0	25
Sodium-4,8-diamino-1,5-dihydroxy-anthraquinone-2,6-disulfonate	—	$2.0 \times 10^{-2}$ – $3.7 \times 10^{-1}$	26
1-Amino-4-hydroxyanthraquinone	—	$1.0 \times 10^{-1}$ – $9.0 \times 10^{-1}$	27
Paracetamol	$1.4 \times 10^{-3}$	$2.8 \times 10^{-2}$ –1.12	29
Sodium hexametaphosphate	$6.0 \times 10^{-3}$	$1.0 \times 10^{-3}$ –60	35
Sodium triphosphate	$9.4 \times 10^{-4}$	$1.0 \times 10^{-3}$ –45	36
Sodium pyrophosphate	$9.5 \times 10^{-3}$	$1.0 \times 10^{-3}$ –30	Present study
Sodium trimetaphosphate	$1.1 \times 10^{-3}$	$1.0 \times 10^{-3}$ –75	Present study
Sodium tetrametaphosphate	$3.8 \times 10^{-3}$	$1.0 \times 10^{-3}$ –70	Present study

dihydroxyanthraquinone-2,6-disulfonate is transformed in strongly acidic medium a pink highly fluorescent product by means of oxygen dissolved in water [26]. This reaction is slow and takes 2 months to reach completion. An another fluorimetric determination of cerium has been accomplished by Salinas *et al.* based on the oxidative reaction between cerium(IV) and 1-amino-4-hydroxyanthraquinone [27]. And a recent study on the fluorimetric determination of cerium(IV) based on the oxidative reaction between cerium(IV) and paracetamol has been reported by Jie *et al.* [29]. The fluorescence intensity of the system reaches a maximum after heating at 100°C for 10 min and then remains stable for 2 h.

In our previous works, we have reported two reagents for the fluorimetric determination of cerium(III) [35,36].

In this study we investigated other compounds containing phosphate groups which show intense fluorescence with cerium(III) as new alternatives for the fluorimetric determination of cerium(III) and report the optimization of the concentration of these phosphate-containing compounds (sodium pyrophosphate, sodium trimetaphosphate, and sodium tetrametaphosphate) for the fluorescent determination of cerium(III) in solution.

Quenching effects of some other lanthanides and some inorganic anions and all the experimental parameters (effect of pH, effect of temperature, stability of fluorescence with time) were also investigated in detail.

The methods have been applied for the determination of cerium(III) in rare earth mixtures with a good accuracy. To make a comparison several of the best methods in the fluorimetric determination of cerium are listed in Table I.

It was found that the methods presented in this work possess advantages over the existing methods with

respect to selectivity, range of determination, simplicity, and speed.

## EXPERIMENTAL

### Apparatus

A Perkin Elmer 204 fluorescence spectrophotometer with a 150-W xenon arc lamp and 10-mm quartz cells were used. The excitation and emission slit widths were 10 nm. The amplifier gain was adjusted according to the fluorescence intensity.

### Reagents

All chemicals were analytical reagent grade and the solutions were prepared with distilled, deionized water. Standard stock solutions of Ce(III) were prepared by dissolving Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Merck). Sodium pyrophosphate, sodium trimetaphosphate, and sodium tetrametaphosphate solutions were prepared by dissolving Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>·10H<sub>2</sub>O (Merck), Na<sub>3</sub>P<sub>3</sub>O<sub>9</sub>·6H<sub>2</sub>O, and Na<sub>4</sub>P<sub>4</sub>O<sub>12</sub>·4H<sub>2</sub>O. Sodium trimetaphosphate [37] and sodium tetrametaphosphate [38] were prepared by synthesis.

### Procedure

Fluorescence measurements of known amounts of Ce(III) in 0.033 g L<sup>-1</sup> sodium pyrophosphate, 41.4 g L<sup>-1</sup> sodium trimetaphosphate, and 0.96 g L<sup>-1</sup> sodium tetrametaphosphate were made at excitation/emission wavelengths of 300/350, 297/340, and 299/352 nm, respectively.

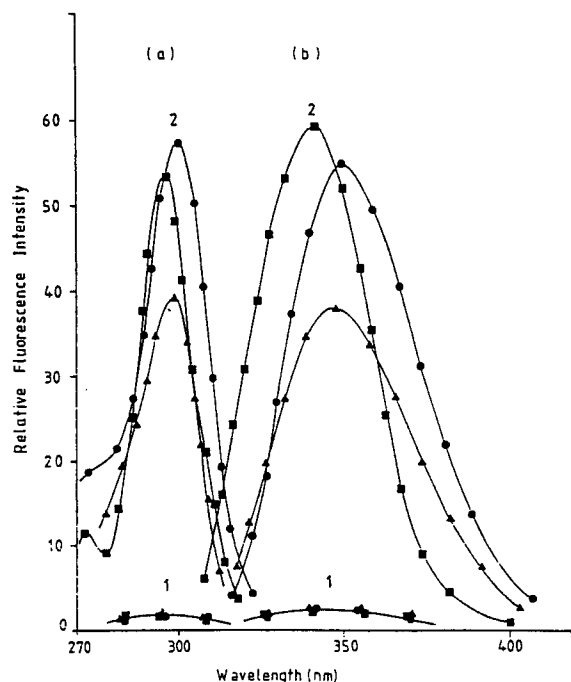


Fig. 1. Fluorescence spectra: (a) excitation; (b) emission. Curves (1):  $7.5 \mu\text{g ml}^{-1}$  Ce(III) without reagents. Curves (2):  $7.5 \mu\text{g ml}^{-1}$  Ce(III) in  $0.033 \text{ g L}^{-1}$  sodium pyrophosphate ( $\blacktriangle$ ); in  $41.4 \text{ g L}^{-1}$  sodium trimetaphosphate ( $\blacksquare$ ); in  $0.96 \text{ g L}^{-1}$  sodium tetrametaphosphate ( $\bullet$ ).

## RESULTS AND DISCUSSION

### Fluorescence Spectra

In pyrophosphate, trimetaphosphate, and tetrametaphosphate solutions, Ce(III) fluoresces strongly when irradiated with ultraviolet radiation. Other lanthanide ions do not show measurable fluorescence under these conditions. The excitation and emission spectra are shown in Fig. 1.

Experimental results showed that Ce(III) ions in sodium pyrophosphate, sodium trimetaphosphate, and sodium tetrametaphosphate solutions are more fluorescent than those in pure aqueous solutions and in the presence of only sulfuric and hydrochloric acid. The results are given in Table II. For sulfuric and hydrochloric acid solutions, optimum acid concentrations given in the literature are used. Table II also shows that high fluorescence intensities come from complexes of Ce(III) with condensed phosphate groups and not from hydrated Ce(III) or hydrolysis of Ce(III).

### Effect of Concentration

The effect of sodium pyrophosphate, sodium trimetaphosphate, and sodium tetrametaphosphate concentrations on the fluorescence intensities were studied for two Ce(III) concentrations (15 and  $0.05 \mu\text{g ml}^{-1}$ ). Fig-

Table II. Comparison of the Fluorescence Intensity of Ce(III) in Different Solutions

Concentration of Ce(III) ( $\mu\text{g ml}^{-1}$ )	Fluorescence intensity			
	In pure aqueous solution	In $39.2 \text{ g L}^{-1}$ $\text{H}_2\text{SO}_4$ solution	In $255.5 \text{ g L}^{-1}$ HCl solution	In $0.033 \text{ g L}^{-1}$ sodium pyrophosphate solution
(a) Excitation and emission wavelengths of 300 and 350 nm, respectively				
7.5	74	155	265	1490
15.0	150	345	532	2920
22.5	232	435	790	4510
(b) Excitation and emission wavelengths of 297 and 340 nm, respectively				
				In $41.4 \text{ g L}^{-1}$ sodium trimetaphosphate solution
7.5	72	160	270	1440
15.0	145	350	540	2880
22.5	228	440	800	4420
(c) Excitation and emission wavelengths of 299 and 352 nm, respectively				
				In $0.96 \text{ g L}^{-1}$ sodium tetrametaphosphate solution
7.5	70	185	300	1584
15.0	140	380	570	3210
22.5	230	500	845	5060

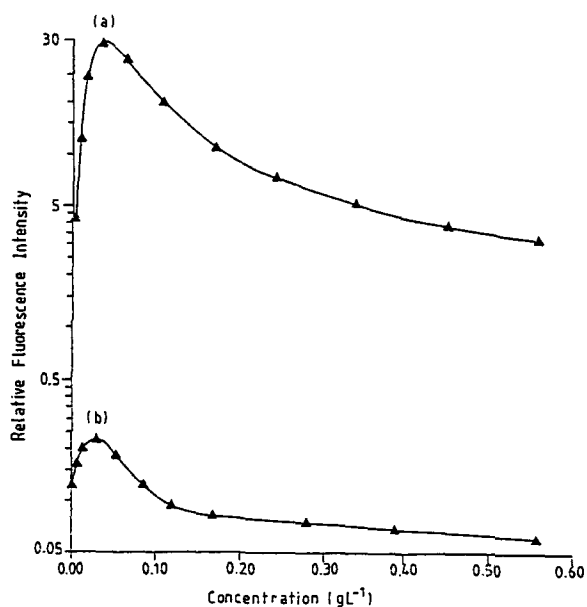


Fig. 2. Variation of fluorescence intensity with sodium pyrophosphate concentrations: (a)  $15 \mu\text{g ml}^{-1}$  Ce(III); (b)  $0.05 \mu\text{g ml}^{-1}$  Ce(III). Excitation wavelength, 300 nm; emission wavelength, 350 nm.

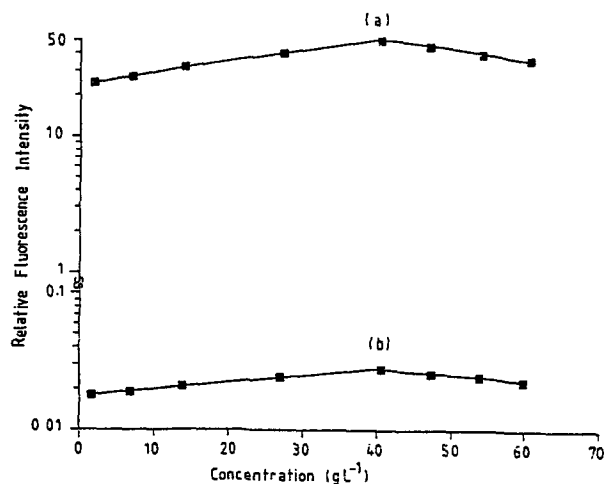


Fig. 3. Variation of fluorescence intensity with sodium trimetaphosphate concentrations: (a)  $15 \mu\text{g ml}^{-1}$  Ce(III); (b)  $0.05 \mu\text{g ml}^{-1}$  Ce(III). Excitation wavelength, 297 nm; emission wavelength, 340 nm.

ures 2, 3, and 4 show that maximum fluorescence intensities were obtained at 0.033, 41.4, and  $0.96 \text{ g L}^{-1}$ , respectively.

#### Stability of Fluorescence with Time

The effect of time on the fluorescence intensities were investigated with 15 and  $0.05 \mu\text{g ml}^{-1}$  Ce(III) in

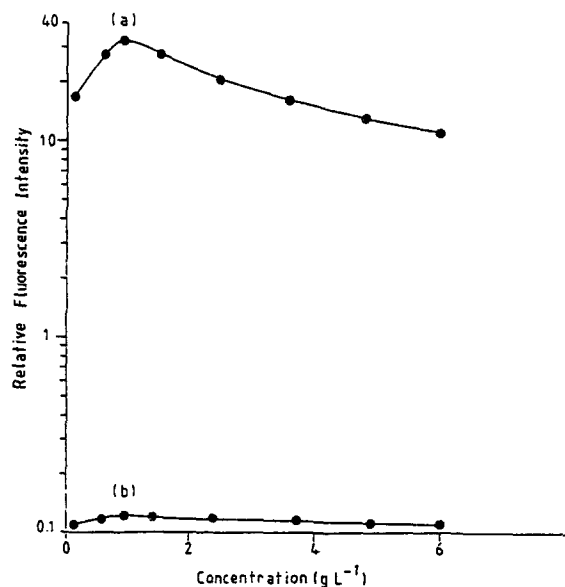


Fig. 4. Variation of fluorescence intensity with sodium tetrametaphosphate concentrations: (a)  $15 \mu\text{g ml}^{-1}$  Ce(III); (b)  $0.05 \mu\text{g ml}^{-1}$  Ce(III). Excitation wavelength, 299 nm; emission wavelength, 352 nm.

$0.033 \text{ g L}^{-1}$  sodium pyrophosphate,  $41.4 \text{ g L}^{-1}$  sodium trimetaphosphate, and  $0.96 \text{ g L}^{-1}$  sodium tetrametaphosphate solutions. As shown in Table III, the fluorescence intensities of these solutions have been found to be stable with time and uninfluenced by light.

#### Effect of pH

The effect of pH was studied in the range of  $-0.2$ – $12.2$  by adjusting the pH with sulfuric acid or sodium hydroxide solutions. The results shown in Fig. 5 indicate that the fluorescence intensities are maximum and constant in the pH range  $5.30$ – $8.95$  for pyrophosphate,  $-0.20$ – $8.00$  for trimetaphosphate, and  $3.70$ – $9.00$  for tetrametaphosphate. After using a series of buffer systems, it was found that borax–hydrochloric acid buffer can be used successfully without causing any quenching. Nevertheless, in these studies no buffer was used because the pH of the solutions was always in the maximum range during the entire procedure.

#### Effect of Temperature

The effect of temperature was studied and it was found that it was not pronounced between  $5$  and  $50^\circ\text{C}$  for pyrophosphate,  $5$  and  $70^\circ\text{C}$  for trimetaphosphate, and  $5$  and  $60^\circ\text{C}$  for tetrametaphosphate. Room temperature is recommended for all measurements.

Table III. Stability of Fluorescence with Time

Reagent	Relative fluorescence intensity											
	Normal fluorimetric measurement						Measurement under continuous irradiation					
	0.05 $\mu\text{g ml}^{-1}$ Ce(III)			15 $\mu\text{g ml}^{-1}$ Ce(III)			0.05 $\mu\text{g ml}^{-1}$ Ce(III)			15 $\mu\text{g ml}^{-1}$ Ce(III)		
	At the beginning	After 1 h	Decrease (%)	At the beginning	After 1 h	Decrease (%)	At the beginning	After 1 h	Decrease (%)	At the beginning	After 1 h	Decrease (%)
In 0.033 g L <sup>-1</sup> sodium pyrophosphate	0.045	0.045	0	33	33	0	0.045	0.039	13.33	33	28.8	12.72
In 41.4 g L <sup>-1</sup> sodium trimetaphosphate	0.620	0.620	0	62	62	0	0.620	0.540	12.90	62	54.3	12.42
In 0.96 g L <sup>-1</sup> sodium tetrametaphosphate	0.600	0.600	0	48	48	0	0.600	0.530	11.67	48	43	10.42

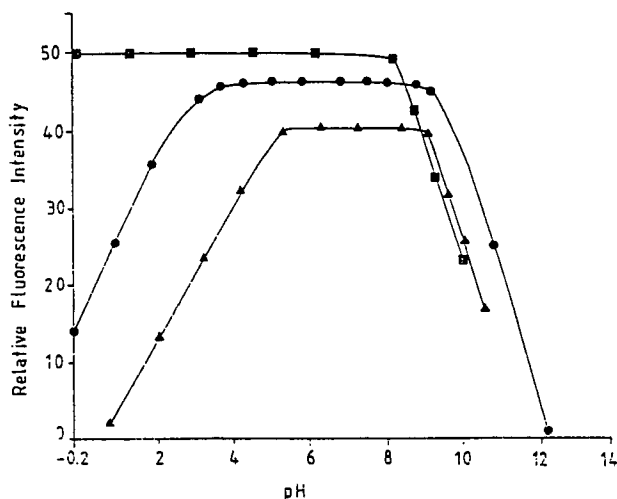


Fig. 5. Effect of pH on the fluorescence intensity: 7.5  $\mu\text{g ml}^{-1}$  Ce(III) in 0.033 g L<sup>-1</sup> sodium pyrophosphate (▲); in 41.4 g L<sup>-1</sup> sodium trimetaphosphate (■); in 0.96 g L<sup>-1</sup> sodium tetrametaphosphate (●).

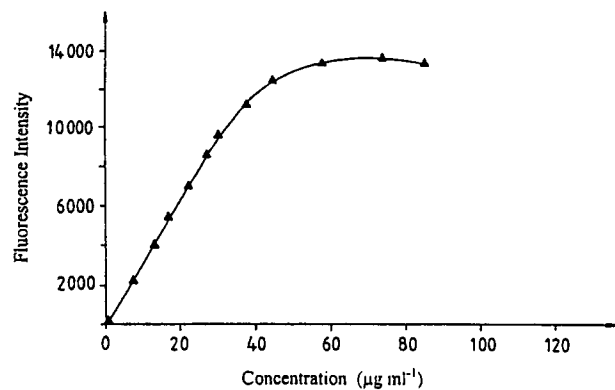


Fig. 6. Fluorescence intensity as a function of the concentration of Ce(III) in 0.033 g L<sup>-1</sup> sodium pyrophosphate solution. Excitation wavelength, 300 nm; emission wavelength, 350 nm.

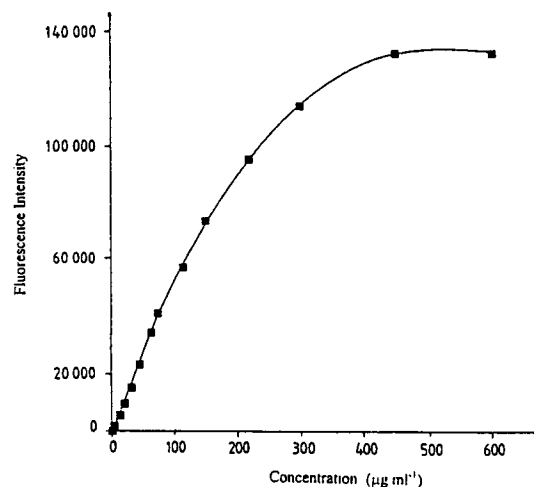


Fig. 7. Fluorescence intensity as a function of the concentration of Ce(III) in 41.4 g L<sup>-1</sup> sodium trimetaphosphate solution. Excitation wavelength, 297 nm; emission wavelength, 340 nm.

### Calibration Graphs

The calibration graphs for the determination of Ce(III) were constructed under optimum conditions. Good linearities were obtained over the ranges 0.001–30  $\mu\text{g ml}^{-1}$  Ce(III) for pyrophosphate (Fig. 6), 0.001–75  $\mu\text{g ml}^{-1}$  Ce(III) for trimetaphosphate (Fig. 7), and 0.001–70  $\mu\text{g ml}^{-1}$  Ce(III) for tetrametaphosphate (Fig. 8). The limits of detection are  $9.5 \times 10^{-3}$   $\mu\text{g ml}^{-1}$  Ce(III),  $1.1 \times 10^{-3}$   $\mu\text{g ml}^{-1}$  Ce(III), and  $3.8 \times 10^{-3}$   $\mu\text{g ml}^{-1}$  Ce(III), respectively. They were calculated by multiplying the standard deviation of 16 blank measurements by 3 and dividing by the slope of the linear calibration curves. From the calibration graphs it was seen that the linear ranges for trimetaphosphate and tetrametaphosphate are larger than those for the methods

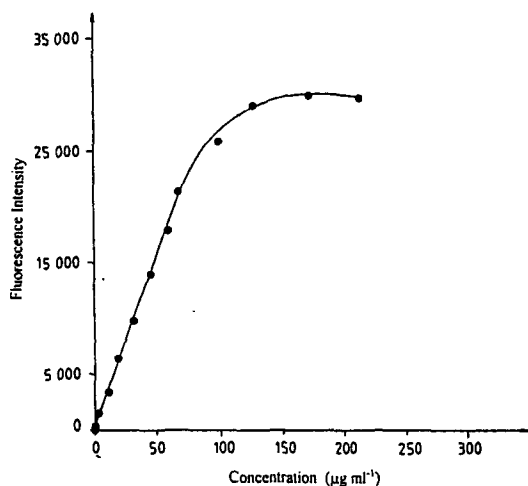


Fig. 8. Fluorescence intensity as a function of the concentration of Ce(III) in 0.96 g L<sup>-1</sup> sodium tetrametaphosphate solution. Excitation wavelength, 299 nm; emission wavelength, 352 nm.

cited in the literature. These results are also shown in Table I.

### Interferences

As shown in Table V, we prepared different mixtures in three media (0.033 g L<sup>-1</sup> sodium pyrophos-

phate, 41.4 g L<sup>-1</sup> sodium trimetaphosphate, and 0.96 g L<sup>-1</sup> sodium tetrametaphosphate) to investigate the effect of other lanthanides on the fluorescence intensities. When the lanthanides were present at the same ratios as in monazite minerale, no interference was observed.

The effects of La(III), Ho(III), Lu(III), and some diverse anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup>) on the fluorescence intensities in these three media are given in Table IV. Ho(III) caused serious interference in 0.033 g L<sup>-1</sup> sodium pyrophosphate solution. Other lanthanide ions show no significant interference at low concentrations. Phosphate ions caused serious interference in all media. But no interference was observed for 300 µg ml<sup>-1</sup> chloride, nitrate, or sulfate ions.

### Application of the Methods

These procedures were applied to the determination of trace amounts of cerium(III) in some synthetic mixtures. The results given in Table V indicate that the proposed methods are suitable and can be successfully applied.

### Precision

The precisions of the determinations were proved by measuring 16 solutions of the same sample 16 times.

Table IV. Percentage Quenching by Some Lanthanides and Anions on the Fluorescence of 15 µg ml<sup>-1</sup> Ce(III)

Reagent: 15 µg ml <sup>-1</sup> Ce(III) in	Ion	Quenching (%)				
		15 µg ml <sup>-1</sup>	30 µg ml <sup>-1</sup>	45 µg ml <sup>-1</sup>	100 µg ml <sup>-1</sup>	300 µg ml <sup>-1</sup>
0.033 g L <sup>-1</sup> sodium pyrophosphate	La (III)	0	8.72	12.85	26.90	79.08
	Ho (III)	40	76.88	—	—	—
	Lu (III)	0	5.46	8.06	17.03	50.92
	Cl <sup>-</sup>	0	0	0	0	0
	NO <sub>3</sub> <sup>-</sup>	0	0	0	0	0
	SO <sub>4</sub> <sup>2-</sup>	0	0	0	0	0
	PO <sub>4</sub> <sup>3-</sup>	50	96.50	—	—	—
41.4 g L <sup>-1</sup> sodium trimetaphosphate	La (III)	0	0	0	13.00	38.50
	Ho (III)	0	0	0	17.20	50.32
	Lu (III)	0	0	0	24.30	72.40
	Cl <sup>-</sup>	0	0	0	0	0
	NO <sub>3</sub> <sup>-</sup>	0	0	0	0	0
	SO <sub>4</sub> <sup>2-</sup>	0	0	0	0	0
	PO <sub>4</sub> <sup>3-</sup>	49.80	97.64	—	—	—
0.96 g L <sup>-1</sup> sodium tetrametaphosphate	La (III)	0	10.1	15.3	34.0	—
	Ho (III)	0	10.0	14.9	33.8	—
	Lu (III)	0	11.0	15.8	34.3	—
	Cl <sup>-</sup>	0	0	0	0	0
	NO <sub>3</sub> <sup>-</sup>	0	0	0	0	0
	SO <sub>4</sub> <sup>2-</sup>	0	0	0	0	0
	PO <sub>4</sub> <sup>3-</sup>	30	58.90	—	—	—

Table V. Analysis of the Synthetic Mixtures

Reagent	Mixture No.	Mixture composition ( $\mu\text{g ml}^{-1}$ )	Ce(III) found ( $\mu\text{g ml}^{-1}$ )	Error (%)
In 0.033 g L <sup>-1</sup> sodium pyrophosphate	1 <sup>a</sup>	Ce(7.50), La(2.50), Pr(0.68), Nd(2.50), Sm(0.26), Eu(0.0075), Gd(0.30), Tb(0.10), Dy(0.12), Ho(0.03), Er(0.06), Yb(0.03), Lu(0.015), Tm(0.001)	7.35	2.00
	2	Ce(10.00), La(3.00), Sm(1.00), Gd(1.00)	9.90	1.00
	3	Ce(15.00), La(5.00), Sm(1.00), Gd(2.00)	14.84	1.07
	4	Ce(20.00), La(7.50), Tb(1.00), Ho(1.00), Tm(1.00)	19.80	1.00
In 41.4 g L <sup>-1</sup> sodium trimetaphosphate	1 <sup>a</sup>	Ce(7.50), La(2.50), Pr(0.68), Nd(2.50), Sm(0.26), Eu(0.0075), Gd(0.30), Tb(0.10), Dy(0.12), Ho(0.03), Er(0.06), Yb(0.03), Lu(0.015), Tm(0.001)	7.40	1.33
	2	Ce(10.00), Nd(5.00), Sm(3.00) Gd(3.00)	9.89	1.10
	3	Ce(15.00), Sm(5.00), Tm(3.00), Yb(2.00), La(5.00)	14.83	1.13
	4	Ce(22.50), La(7.50), Nd(7.50), Sm(1.00)	22.22	1.24
In 0.96 g L <sup>-1</sup> sodium tetrametaphosphate	1 <sup>a</sup>	Ce(7.50), La(2.50), Pr(0.68), Nd(2.50), Sm(0.26), Eu(0.0075), Gd(0.30), Tb(0.10), Dy(0.12), Ho(0.03), Er(0.06), Yb(0.03), Lu(0.015), Tm(0.001)	7.38	1.60
	2	Ce(10.00), La(3.00), Sm(1.00), Tm(1.00), Gd(1.00)	9.86	1.40
	3	Ce(15.00), La(3.00), Ho(3.00), Sm(2.00), Tm(1.00)	14.80	1.33
	4	Ce(22.50), Gd(1.00), Tm(1.00), Sm(2.00), La(3.00), Nd(3.00)	22.18	1.42

<sup>a</sup>These mixtures were prepared on the basis of relative concentrations of rare earths in monazite minerale.

The coefficients of variation of these measurements were 1.1% for 15  $\mu\text{g ml}^{-1}$  and 1.2% for 0.05  $\mu\text{g ml}^{-1}$  Ce(III) in 0.033 g L<sup>-1</sup> sodium pyrophosphate solutions, 1% for 15  $\mu\text{g ml}^{-1}$  and 1.1% for 0.05  $\mu\text{g ml}^{-1}$  Ce(III) in 41.4 g L<sup>-1</sup> sodium trimetaphosphate solutions, and 1.2% for 15  $\mu\text{g ml}^{-1}$  and 1.3% for 0.05  $\mu\text{g ml}^{-1}$  Ce(III) in 0.96 g L<sup>-1</sup> sodium tetrametaphosphate solutions.

## CONCLUSION

As the results of this study show, trace determinations of Ce(III) with sodium pyrophosphate, sodium trimetaphosphate, and sodium tetrametaphosphate solutions are three simple, sensitive, and selective new alternatives to the methods found in the literature for direct fluorimetric determinations of Ce(III).

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