Complexation Reactions of Cerium(III and IV) with 9-Phenyl-2,3,7- trihydroxy-6-fluorone in the Presence of Cationic Surfactants

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Abstract. The complexation reactions of cerium(III and IV) with 9-phenyl-2,3,7-trihydroxy-6-fluorone (H_3PF) have been studied in the presence and absence of some surfactants and protective colloids. Maximum enhancement of the chelate absorbances is obtained with the cationic surfactant cetylpyridinium bromide (*CPB*) or cetyltrimethylammonium bromide (*CTAB*). In the *pH* ranges 8.2−9.0 and 9.8−10.8 the ternary 1:3:3 and 1:4:3 cerium(III)-PF-CPB complexes are formed with molar absorptivities of 9.02×10^4 and $9.86 \cdot 10^4 \, \mathrm{l \, mol^{-1} \, cm^{-1}}$ at 570 and 590 nm, respectively. The corresponding 1:4:2 and 1:3:2 complexes of cerium(IV) are formed in the *pH* ranges 8.4−9.0 and 9.8−10.6 in the presence of *CTAB* and *CPB*, respectively. Their molar absorptivities are $8.00 \cdot 10^4$ and $8.56 \cdot 10^4 \, \mathrm{l \, mol^{-1} \, cm^{-1}}$ at 570 and 590 nm, respectively. The stability constants of the studied complexes have been determined and a spectrophotometric method has been developed to determine the cerium content in monazite concentrate.

Keywords. Cerium(III and IV) complexes; 9-Phenyl-2,3,7-trihydroxy-6-fluorone; Surfactants.

Komplexierungsreaktionen von Cer(III und IV) mit 9-Phenyl-2,3,7-trihydroxy-6-fluoron in Gegenwart kationischer oberflächenaktiver Stoffe

Zusammenfassung. Es wurden Komplexierungsreaktionen von Cer(III und IV) mit 9-Phenyl-2,3,7-trihydroxy-6-fluoron (H_3PF) in Gegenwart und auch ohne oberflächenaktive Stoffe und Schutzkolloide untersucht. Maximale Verstärkung der UV-VIS-Absorption wurde mit den kationischen oberflächenaktiven Verbindungen Cetylpyridiniumbromid (*CPB*) und Cetyltrimethylammoniumbromid (*CTAB*) erreicht. Im *pH*-Bereich von 8.2−9.0 und 9.8−10.8 bildeten sich die ternären 1:3:3 und 1:4:3 Cer(III)-*PF*-*CPB*-Komplexe mit molaren Extinktionskoeffizienten von $9.02 \cdot 10^4$, bzw. $9.86 \cdot 10^4 \, \mathrm{l \, mol^{-1} \, cm^{-1}}$ bei 570 bzw. 590 nm. Die entsprechenden 1:4:2 und 1:3:2 Cer(IV)-Komplexe wurden im *pH*-Bereich 8.4−9.0 und 9.8−10.6 in Gegenwart von *CTAB* und *CPB* gebildet, wobei die Extinktionskoeffizienten bei $8.00 \cdot 10^4$, bzw. $8.56 \cdot 10^4 \, \mathrm{l \, mol^{-1} \, cm^{-1}}$ bei 570 bzw. 590 nm lagen. Es wurden die Stabilitätskonstanten der Komplexe bestimmt und es wurde eine spektrophotometrische Methode zur Bestimmung von Cer in Monazitkonzentrat entwickelt.

Introduction

The enhancement (sensitization) of color reactions of metal ions with chromogenic reagents by the presence of surfactants provides an inexpensive way for determining

low concentrations of elements. The change in color produced in the presence of a surfactant is attributed to an interaction of the binary complex with the surfactant to build up a true ternary complex, adsorption of the binary complex on the micelles of surfactant, or formation of micelles followed by interaction of the binary complex with the surfactant ion to form an ion-association complex [1].

The present work was carried out to investigate the reactions of cerium(III and IV) ions with 9-phenyl-2,3,7-trihydroxy-6-fluorone (H$_3$PF) in the presence and absence of different types of surfactants and protective colloids. The stoichiometry of the formed complexes and their stability constants were determined. Maximum sensitization of the color reactions was obtained in the presence of cationic surfactants. Consequently, highly sensitive spectrophotometric methods for cerium determination were developed and used to determine the cerium content in monazite concentrate.

Experimental Part

All chemicals were of analytical reagent purity. Surfactants and protective colloids were used as received without further purification. Bi-distilled water was used throughout. Stock solutions ($1 \cdot 10^{-2} M$) of cerium(III) and cerium(IV) were prepared by dissolving 1.0856 g of cerium(III) nitrate hexahydrate in water containing 1 ml of nitric acid, or 0.4303 g of cerium(IV) oxide in 10 ml of 1 : 1 hydrochloric acid and diluted to 250 ml with water in a volumetric flask. These solutions were standardized with EDTA [2]. H$_3$PF was purified and a $1 \cdot 10^{-3} M$ solution was prepared according to Marczenko et al. [3]. Borax buffer solutions of different pH values were prepared by adjusting the pH of $5 \cdot 10^{-2} M$ borax solution with hydrochloric acid or sodium hydroxide solution to the desired value. Cationic and anionic surfactants were prepared as $1 \cdot 10^{-2} M$ solutions whereas nonionic surfactants and protective colloids were utilized as 5% v/v and 0.5% m/v, respectively.

A Perkin-Elmer Model Lambda 3B double-beam UV-visible spectrophotometer equipped with matched 1-cm quartz cells was used for optical measurements. A Schott Geräte pH-meter Model CG 710 fitted with a combined glass-calomel electrode was used for pH adjustment.

Determination of Cerium(III) with H$_3$PF *and CPB at pH 8.6 or 10.2*

Introduce a suitable aliquot of sample solution containing up to 42 μg of cerium(III), 2.5 ml of H$_3$PF solution and 5 ml of CPB solution into 25 ml volumetric flask. Complete the volume to the mark with borax buffer of pH 8.6 or 10.2 and measure the absorbance after 30 minutes of mixing at 570 or 590 nm, respectively. Determine the cerium content using calibration graphs prepared in the same manner.

Determination of Cerium(IV) with H$_3$PF *and CTAB or CPB*

Transfer up to 47 μg of cerium(IV) into a 25 ml volumetric flask. Add 2.5 ml of H$_3$PF solution and 5 ml of CTAB or CPB solution. Complete to volume with borax buffer of pH 8.8 or 10.2, respectively. Let stand for 45 min and measure the absorbance against a blank at 570 or 595 nm, respectively.

Results and Discussion

Tables 1 and 2 illustrate the results obtained for the effect of some protective colloids and surfactants on the spectral characteristics of cerium(III and IV)-PF complexes at pH 8.6(8.8) and 10.2. Maximum enhancement of the absorbance of cerium(III) complex was obtained at pH 8.6 and 10.2 in the presence of CPB. On the other

Table 1. Effect of surfactants and protective colloids on the absorbance of cerium(III)phenylfluorone complex at pH 8.6 and 10.2. Ce $5.66 \cdot 10^{-6}$ M; phenylfluorone $1.2 \cdot 10^{-4}$ M; surfactant $2 \cdot 10^{-3}$ M (1% for nonionic surfactants and 0.1% for protective colloids); 1-cm cells

Surfactant or protective Colloid*	Type	At pH 8.6			At pH 10.2		
		λ_{max} (nm)	Absorb.	$\varepsilon \cdot 10^4$ l mol^{-1} cm^{-1}	λ_{max} (nm)	Absorb.	$\varepsilon \cdot 10^4$ l mol^{-1} cm^{-1}
Without	–	525	0.188	3.32	550	0.175	3.09
SLS	anionic	525	0.181	3.20	555	0.260	4.59
SAS	anionic	520	0.065	1.15	545	0.341	6.02
Emulsifier S	nonionic	540	0.258	4.56	555	0.356	6.29
Tween 40	nonionic	530	0.265	4.68	560	0.388	6.86
Tween 60	nonionic	510	0.200	3.53	560	0.416	7.35
Tween 80	nonionic	538	0.303	5.36	550	0.445	7.86
Triton X-100	nonionic	550	0.250	4.42	562	0.367	6.48
CTAB	cationic	560	0.500	8.83	585	0.487	8.60
CPB	cationic	570	0.511	9.02	590	0.558	9.86
CPC	cationic	570	0.500	8.83	590	0.397	7.01
Zephiramine	cationic	560	0.460	8.13	585	0.412	7.28
Gelatin	prot. colloid	525	0.262	4.63	550	0.220	3.89
Polyvinylpyrrolidone	prot. colloid	530	0.495	8.75	565	0.405	7.16
Poly(vinyl alc.)	prot. colloid	538	0.355	6.27	540	0.388	6.86

* *SLS*, sodium lauryl sulfate; *SAS*, sodium alkylbenzene sulfonate; Emulsifier S, ethoxylated fatty alcohol; Tween 40, polyoxyethylene sorbitan monopalmitate; Tween 60, polyoxyethylene sorbitan monostearate; Tween 80, polyoxyethylene sorbitan monooleate; Triton X-100, polyoxyethylene-*p-tert*-octylphenol; *CTAB*, cetyltrimethyammonium bromide; *CPB*, cetylpyridinium bromide; *CPC*, cetylpyridinium chloride; Zephiramine, benzyldimethyltetradecylammonium chloride

Table 2. Effect of surfactants and protective colloids on the absorbance of cerium(IV)-phenylfluorone complex at pH 8.8 and 10.2. Ce $7.71 \cdot 10^{-6} M$; other conditions as in Table 1

Surfactant or protective Colloid	At pH 8.8			At pH 10.2		
	λ_{max} (nm)	Absorb.	$\varepsilon \cdot 10^4$ l mol^{-1} cm^{-1}	λ_{max} (nm)	Absorb.	$\varepsilon \cdot 10^4$ l mol^{-1} cm^{-1}
Without	530	0.302	3.92	550	0.265	3.44
SLS	535	0.195	2.53	555	0.285	4.06
SAS	–	–	–	560	0.240	3.42
Emulsifier S	500	0.530	6.87	560	0.436	6.22
Tween 40	530	0.275	3.57	565	0.573	8.17
Tween 60	535	0.515	6.68	555	0.490	6.98
Tween 80	545	0.250	3.24	565	0.490	6.98
Triton X-100	535	0.342	4.44	555	0.484	6.90
CTAB	570	0.617	8.00	590	0.557	7.94
CPB	575	0.556	7.21	595	0.600	8.56
CPC	575	0.560	7.26	595	0.590	8.41
Zephiramine	570	0.520	6.75	592	0.508	7.24
Gelatin	535	0.316	4.10	555	0.410	5.85
Polyvinylpyrrolidone	535	0.530	6.88	545	0.580	8.27
Poly(vinyl alcohol)	535	0.350	4.54	550	0.485	6.92
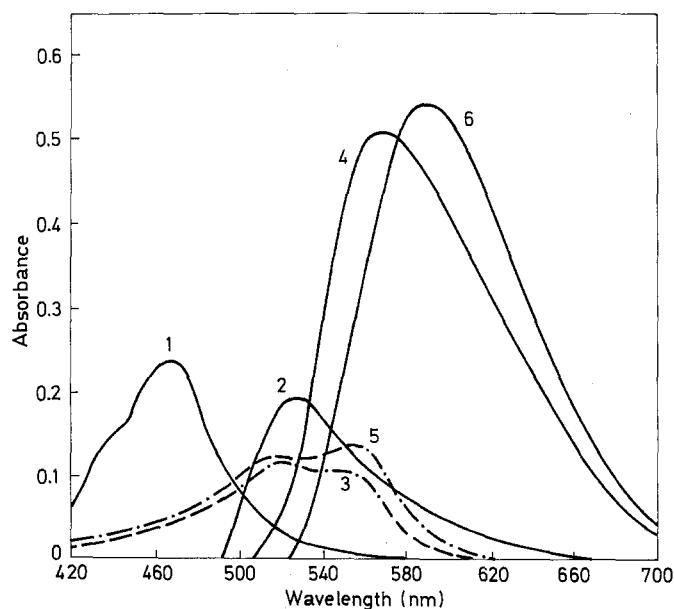
Fig. 1. Absorption spectra of cerium(III) complexes in aqueous and aqueous micellar media. $[Ce^{3+}] = 5.66 \cdot 10^{-6} M$; $[CPB] = 2 \cdot 10^{-3} M$; [Phenylfluorone] $= 7.5 \cdot 10^{-6} M$ for curves 1, 3 and 5, $1.2 \cdot 10^{-4} M$ for curves 4 and 6, and $2 \cdot 10^{-4} M$ for curve 2; 1-cm cell. *1* Phenylfluorone at pH 8.4 vs. buffer; *2* cerium-phenylfluorone binary complex vs. blank; *3* phenylfluorone + CPB at pH 8.6 vs. blank; *4* cerium-phenylfluorone-CPB ternary complex at pH 8.6 vs. blank; *5* Phenylfluorone + CPB at pH 10.2 vs. blank; *6* cerium-phenylfluorone-CPB ternary complex at pH 10.2 vs. blank
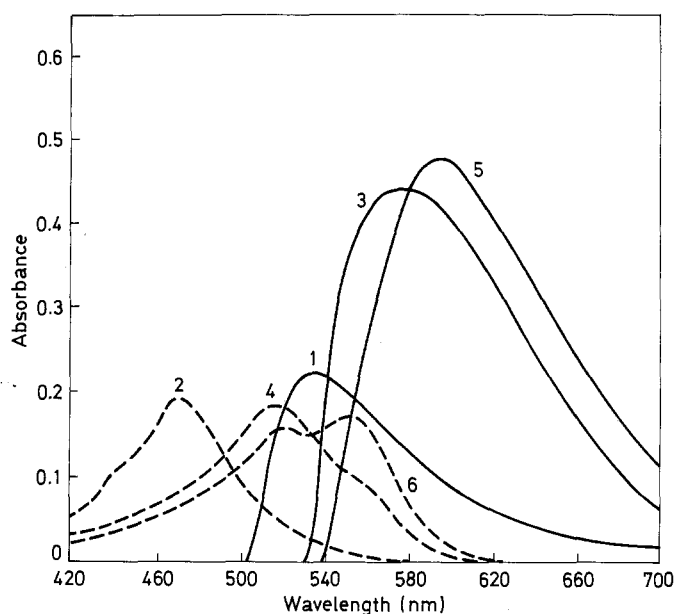
Fig. 2. Absorption spectra of cerium(IV) complexes in aqueous and aqueous micellar media. $[Ce^{4+}] = 5.60 \cdot 10^{-6} M$; $[CTAB] = [CPB] = 2 \cdot 10^{-3} M$; $[Phenylfluorone] = 8 \cdot 10^{-6} M$ for curves 2, 4 and 6, and $2 \cdot 10^{-4} M$ for curves 1, 3 and 5; 1-cm cell. *1* cerium-phenylfluorone binary complex vs. blank; *2* phenylfluorone at pH 9.4 vs. buffer; *3* cerium-phenylfluorone-*CTAB* ternary complex at pH 8.8 vs. blank; *4* phenylfluorone + *CTAB* at pH, 8.8 vs. blank; *5* cerium-phenylfluorone-*CPB* at pH 10.2 vs. blank; *6* phenylfluorone + *CPB* at pH 10.2 vs. blank

hand, *CTAB* and *CPB* were optimum sensitizers for the color reactions of cerium(IV) at pH 8.8 and 10.2, respectively.

Spectral Characteristics

The absorption spectra of cerium(III)-*PF* complexes formed in the absence and presence of *CPB* are shown in Fig. 1. The binary complex formed at pH 8.4 in the absence of surfactant exhibits an absorption maximum at 525 nm (curve 2). The corresponding reagent blank absorbs at 470 nm (curve 1). Addition of *CPB* to the reagent at pH 8.6 is accompanied by batho- and hypochromic shifts (curve 3). At the latter pH, the absorption maximum of the complex is shifted to 570 nm and the absorbance increases 3-fold as a result of the sensitizing action of *CPB* (curve 4). At pH 10.2 in the presence of *CPB* the complex absorption maximum is shifted to 590 nm with further increase in the absorbance value (curve 6). The spectral curve of the blank is given in curve 5.

In Fig. 2, curves 1 and 2 show the spectral curves of the cerium(IV) binary complex and its reagent blank at pH 9.4. Their absorption maxima are at 535 and 470 nm, respectively. In the presence of *CTAB* at pH 8.8 the complex has an absorption maximum at 570 nm (curve 3) and the blank at 520 nm (curve 4). Moreover, in the presence of *CPB* at pH 10.2 the absorption maximum of the complex is shifted to 595 nm with further increase of absorbance (curve 5). The blank spectrum is shown in curve 6.

Effect of pH

The effect of *pH* on the formation of cerium(III and IV) binary and sensitized complexes was investigated using $7.5 \cdot 10^{-6} M$ of the metal ion, $2 \cdot 10^{-4} M$ of reagent $(1 \cdot 10^{-4} M$ in the presence of surfactant) and $2 \cdot 10^{-3} M$ surfactant as final concentrations. The *pH* was adjusted with diluted hydrochloric acid or sodium hydroxide solution.

The binary cerium(III) complexes have maximum and constant absorbances in the *pH* ranges $8.2 - 8.8$ and $10.0 - 10.6$ at 525 and 550 nm, respectively. The sensitized complexes with *CPB* are formed in the *pH* ranges $8.2 - 9.0$ and $9.8 - 10.8$, at 570 and 590 nm, respectively. The corresponding *pH* ranges of cerium(IV) binary complexes are $8.8 - 9.5$ and $10.1 - 10.7$ at 535 and 550 nm, whereas the sensitized complexes with *CTAB* and *CPB* are formed in the *pH* ranges $8.4 - 9.0$ and $9.8 - 10.6$ at 570 and 595 nm, respectively. At the optimum *pH* ranges no difference in the absorbance values of the complexes are noticed when borax buffer is used. Thus, borax buffer is utilized for *pH* adjustment in the procedures.

Effect of Reagent and Surfactant Concentrations

The optimum concentration ranges of H_3PF for the formation of cerium(III and IV) binary complexes are $1.2 \cdot 10^{-4} - 2.8 \cdot 10^{-4}$ and $1.6 \cdot 10^{-4} - 2.4 \cdot 10^{-4} M$. The corresponding reagent concentration ranges for the formation of the sensitized cerium(III) complexes at *pH* 8.6 and 10.2 are $4.8 \cdot 10^{-5} - 1.8 \cdot 10^{-4}$ and $6 \cdot 10^{-5} - 1.2 \cdot 10^{-4} M$. Moreover, $6.4 \cdot 10^{-5} - 1.6 \cdot 10^{-4}$ and $5.8 \cdot 10^{-5} - 1.3 \cdot 10^{-4} M$ reagent are optimum for the sensitized cerium(IV) complexes with *CTAB* and *CPB*, respectively.

A study of the effect of surfactant concentration on the absorbance of the ternary cerium(III) complexes at *pH* 8.6 and 10.2 reveal maximum enhancement in the presence of $1.2 \cdot 10^{-3} - 3.2 \cdot 10^{-3}$ and $8 \cdot 10^{-4} - 4 \cdot 10^{-3} M$ *CPB*. Moreover, $1.6 \cdot 10^{-4} - 2.8 \cdot 10^{-3}$ and $2.0 \cdot 10^{-4} - 3.2 \cdot 10^{-3} M$ of *CTAB* and *CPB* are optimum for sensitizing cerium(IV) complexes.

Effect of Time

Full color development is obtained after 20 minutes of mixing for cerium(III) binary and ternary complexes. The absorbance of these complexes then remains maximum and constant for 3 hours. Therefore, a standing time of 30 minutes is recommended in the procedures of cerium(III) determination.

On the other hand, the absorbance of cerium(IV) binary complexes reach their maximum values within 50 minutes, whereas the corresponding time for the sensitized complexes is 35 minutes. The complexes are stable for more than 4 hours. In the recommended procedures 45 minutes standing time is selected.

Calibration Curves, Sensitivity and Precision of the Methods

The calibration curves for cerium(III) determination as ternary complexes at *pH* 8.6 and 10.2 adhere to Beer's law up to 1.68 and 1.60 ppm of cerium, respectively. The corresponding curves for cerium(IV) determination as sensitized complexes with *CTAB* and *CPB* are rectilinear up to 1.88 and 1.92 ppm of cerium.

The molar absorptivities of cerium(III)-PF-CPB ternary complexes, formed at pH 8.6 and 10.2, are $9.02 \cdot 10^4$ and $9.86 \cdot 10^4 \, \mathrm{lmol^{-1} \, cm^{-1}}$ at 570 and 590 nm. The molar absorptivities of cerium(IV)-PF-$CTAB$ and cerium(IV)-PF-CPB complexes are $8.00 \cdot 10^4$ and $8.56 \cdot 10^4 \, \mathrm{lmol^{-1} \, cm^{-1}}$ at 570 and 595 nm.

The developed methods for cerium determination are more sensitive than the widely used spectrophotometric procedure utilizing Arsenazo III ($\varepsilon = 5.6 \cdot 10^4$ at 650 nm) [4], 8-hydroxyquinoline ($\varepsilon = 6.7 \cdot 10^3$ at 495 nm) [5], formaldoxime ($\varepsilon = 4.7 \cdot 10^3$ at 340 nm) [6] 3-thianaphthenoyltrifluoroacetone ($\varepsilon = 5.5 \cdot 10^3$ at 424 nm) [7] and tetron ($\varepsilon = 2.5 \cdot 10^4$ at 470 nm) [8].

The sensitivity indices of the developed methods for cerium(III) determination in the presence of CPB at pH 8.6 and 10.2 are 1.55 and 1.42 ng cm^{-2}, respectively. The corresponding values for cerium(IV) determination in presence of $CTAB$ and CPB are 1.75 and 1.64 ng cm^{-2}.

The precision of the proposed procedures was established from the results of ten determinations each of a standard solution containing $4.25 \cdot 10^{-6} M$ of cerium(III) or $3.86 \cdot 10^{-6} M$ of cerium(IV). The standard deviation values for the methods of cerium(III) determination in the presence of CPB at pH 8.6 and 10.2 were 0.0014 and 0.0015. The corresponding values for cerium(IV) determination in the presence of $CTAB$ and CPB were 0.0013 and 0.0011, respectively.

Stoichiometry and Stability Constant of the Complexes

Cerium(III and IV) react with H_3PF in the absence and presence of surfactant to form different types of complexes depending on the pH of the medium. The continuous-variation and slope-ratio methods were used at the optimum pHs, to determine the metal:reagent ratio in the complexes, whereas the iso-molar ratio method [9] was utilized to determine the metal:surfactant ratio.

In aqueous medium, at pH ca. 8, the reagent is a singly charged anion ($pKa = 7$) [10] and reacts with cerium(III) to form the bis complex.

$$\mathrm{Ce(OH)}_n^{\,3-n} + 2\,\mathrm{H_2}PF^- = \mathrm{Ce(H_2}PF)_2\mathrm{(OH)}_x^{\,3-2-x}$$
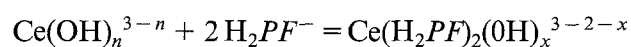
Increasing the pH to ca. 10 enhances the deprotonation of the second proton of reagent and hence the formation of the more stable tris complex.

In case of cerium(IV), the tris complex is formed at lower pH as a result of cationic charge increase. Increasing the pH to ca. 10, though is accompanied by further deprotonation of the ligand, the high hydrolytic tendency of the cation leads to the formation of the mixed hydroxo-bis chelate.

On the other hand, tetrapropylammonium bromide, which is a nondetergent quaternary ammonium salt, exerted a sensitizing action on the absorbance of cerium(III and IV) binary complexes. Consequently, the enhancement of binary complex absorbances with cationic surfactants is due to the formation of true ternary complexes [11, 12].

In the presence of surfactants, the metal:ligand ratios for cerium(III) ternary complexes were 1:3 and 1:4 at pH values 8.6 and 10.2, respectively, whereas for cerium(IV) the corresponding ratios in the presence of $CTAB$ and CPB were 1:4 and 1:3. The obtained increase of metal:ligand ratios in the presence of surfactants is in agreement with previously reported measurements [13, 14].

Table 3. Composition of the binary and ternary complexes and their overall formation constants

	Cerium(III) complexes					Cerium(IV) complexes				
	pH	λ_{max}	$\varepsilon\,1\,mol^{-1}\,cm^{-1}$	$M{:}L$	$\log\beta$	pH	λ_{max}	$\varepsilon\,1\,mol^{-1}\,cm^{-1}$	$M{:}L$	$\log\beta$
In the absence of surfactant	8.4	525	$3.32\cdot10^4$	$1{:}2$	26.2	9.4	535	$3.92\cdot10^4$	$1{:}3$	29.7
	10.2	550	$3.09\cdot10^4$	$1{:}3$	29.5	10.2	550	$3.44\cdot10^4$	$1{:}2$	26.8
				$M{:}L{:}S^*$					$M{:}L{:}S^*$	
In the presence of surfactant	8.6	570	$9.02\cdot10^4$	$1{:}3{:}3$	30.4	8.8	570	$8.00\cdot10^4$	$1{:}4{:}2$	34.4
	10.2	590	$9.86\cdot10^4$	$1{:}4{:}3$	34.1	10.2	595	$8.56\cdot10^4$	$1{:}3{:}2$	30.6

* S, surfactant cation

Table 4. Effect of foreign ions on the determination of cerium(III) and cerium(IV) with phenylfluorone and *CPB* at *pH* 10.2. Ce^{3+} or Ce^{4+}, $4\cdot10^{-6}\,M$; 100-fold molar excess of metal added relative to cerium

Ion added	Ce(III) system		Ce(IV) system	
	Absorbance	Interference (%)	Absorbance	Interference (%)
Without	0.394	−	0.342	−
Al(III)	0.769	+ 95.1	0.798	+ 133.3
As(V)	0.396	+ 0.5	0.330	− 3.5
Ba(II)	0.390	− 1.0	0.347	+ 1.5
Be(II)	0.402	+ 2.0	0.351	+ 2.6
Cr(III)	1.110	+ 181.7	1.081	+ 216.1
Cu(II)	1.091	+ 176.9	1.211	+ 254.1
Fe(III)	1.388	+ 305.8	1.186	+ 226.3
Hg(II)	1.620	+ 311.2	1.593	+ 365.8
La(III)	0.962	+ 144.2	0.937	+ 173.9
Mg(II)	0.937	+ 137.8	1.025	+ 199.7
Mn(II)	1.872	+ 375.1	1.943	+ 468.1
Mo(VI)	0.723	+ 83.5	0.643	+ 88.0
Pb(II)	0.978	+ 148.2	0.841	+ 145.9
Pr(III)	0.937	+ 137.8	0.987	+ 188.6
Sm(III)	1.123	+ 185.0	1.023	+ 199.1
Th(IV)	1.978	+ 402.0	1.963	+ 474.0
V(V)	0.860	+ 118.2	0.808	+ 136.2
U(VI)	1.653	+ 319.2	1.935	+ 465.8
Zr(IV)	0.616	+ 56.3	0.700	+ 75.4

The number of cationic surfactant associated with the formed complexes were 3 and 2 for cerium(III and IV) complexes, irrespective of the medium *pH*. A summary of all the results obtained along with the overall formation constants of the complexes as determined by the continuous-variation method [15] is given in Table 3.

Table 5. Results for cerium content in monazite

Cerium content, %		
This method[a]	Arsenazo III method[b]	X-Ray fluorescence spectrometry
14.17 (mean = 14.42)	14.49 ± 0.22	14.37
14.25		
14.36		
14.42		
14.45		
14.53		
14.56		
14.64		

[a] Standard deviation = 0.15
[b] Six determinations

Interference Study

Several metal ions react with H_3PF to give colored complexes. The influence of 100-fold molar excess of some metal ions on the determination of cerium(III or IV) in the presence of *CPB* at *pH* 10.2 is illustrated in Table 4.

Moreover, a study of the effect of some masking agents on the color reactions show that up to a 1 000-fold molar excess of bromide, iodide, thiosulfate, and thiourea, and up to a 600-fold excess of cyanide, oxalate, tartrate, citrate, and malonate do not interfer. However, these masking agents slightly improved the selectivity of the developed procedures. Consequently, a preliminary separation step of cerium is necessary when present in a complex matrix.

Application of the Method

The proposed procedure for cerium(IV) determination as the *PF-CPB* complex at *pH* 10.2 was used to determine the cerium content in monazite concentrate. A small portion of the finely powdered monazite sample was weighed and digested for 4 hours with concentrated sulfuric acid in a reflux apparatus [16]. The sample solution was evaporated to a small volume and carefully diluted with water. The solution was filtered and further diluted to a suitable volume. Cerium was separated from other matrix elements by extracting cerium(IV) from nitric acid solution into isobutyl methyl ketone [17], stripping in water and determined by the recommended procedure.

The results obtained are given in Table 5. The cerium content in monazite, as determined by the developed procedure, is in good accordance with that obtained by the spectrophotometric method utilizing Arsenazo III and by x-ray fluorescence spectrometry.

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