

THE FLUORIMETRIC DETERMINATION OF CERIUM AND TERBIUM

Záviš HOLZBECHER

Prague Institute of Chemical Technology, 166 28 Prague 6

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It has been found that phosphoric acid decreases the first excitation maximum of Ce(III) at 256 nm, increases the second excitation maximum at 297 nm and shifts the fluorescence maximum from 350 to 346 nm. Under optimum conditions, with $\lambda_{\text{exc}} = 297$ nm and $\lambda_{\text{em}} = 346$ nm, Ce(III) can be determined fluorimetrically with a detection limit of 1.2 ng ml^{-1} in $12\text{M-H}_3\text{PO}_4$ medium. No interference was observed from a 20–200 fold excess of HCl, H_2SO_4 , Na, K, NH_4^+ , Al and the rare earth elements. HNO_3 interferes and Ce(IV) and Fe(III) interfere strongly. It follows from the stereofluorograms of Ce and Tb that the spectra of the two elements are practically independent. The detection limit for Tb(III) in $0.02\text{--}2.5 \text{ M-H}_2\text{SO}_4$ medium for $\lambda_{\text{exc}} = 222$ nm and $\lambda_{\text{em}} = 494$ nm is 33 ng ml^{-1} . No interference was observed from a 5–20 fold excess of Al^{3+} and the other rare earth elements. The determination is slightly less sensitive in H_3PO_4 or HCl medium. The relative standard deviation of the measurement for 10 ng ml^{-1} Ce(III) or 50 ng ml^{-1} Tb(III) is about 3%.

For a number of years, the fluorometric determination of trace amounts of cerium in solution has been carried out in sulfuric or perchloric acid^{1–4}. Solutions are irradiated with radiation corresponding to the first excitation maximum at a wavelength of 255–260 nm and the secondary radiation at a wavelength of the fluorescence maximum of 350–355 nm is measured. The detection limit is about 100 ng ml^{-1} Ce(III).

Terbium has similarly been determined with various detection limits, for example in dimethylformamide (detection limit $157 \text{ } \mu\text{g ml}^{-1}$, ref.⁵), HCl ($5 \text{ } \mu\text{g ml}^{-1}$, ref.⁶), K_2CO_3 (300 ng ml^{-1} , ref.⁷), $\text{K}_2\text{C}_2\text{O}_4$ (50 ng ml^{-1} , ref.⁸), gelatine (100 ng ml^{-1} , ref.⁹) and also as the complex with pivaloyltrifluoroacetone (16 ng ml^{-1} , ref.¹⁰) and by laser fluorimetry as the complex with 1,1,1-trifluoro-5,5-dimethyl-2,4-hexandione (3 pg ml^{-1} , ref.¹¹).

Phosphoric acid is used to increase the fluorescence flux of U(VI) in solution^{12,13}. This work is a study of whether the favourable effect of phosphoric acid can be extended to cerium and terbium.

EXPERIMENTAL

Chemicals and Instruments

All the metal salts and acids employed were of "pro analysi" purity. Cerium (III) chloride was the product of E. Merck (Darmstadt, F.R.G.) and the salts of the other rare earth elements were the products of ICN-K&K Laboratories (Plainview, N.Y., U.S.A.) and Soyuzreaktiv (U.S.S.R.); Tb_4O_7 , Lu_2O_3 (Soyuzreaktiv, U.S.S.R.) and Eu_2O_3 (Johnson Matthey, England) were dissolved by heating in HCl. Deionized water was employed to prepare the solutions. The contents of Ce(III) and Tb(III) in the 0.01 M chloride stock solutions were determined chelometrically¹⁴. Solutions of the required concentration were prepared by diluting the stock solutions with $10^{-3}M$ -HCl.

The fluorescence standard for comparison purposes was a $10^{-6}M$ solution of quinine sulfate, $(C_{20}H_{24}N_2O_2)_2 \cdot H_2SO_4 \cdot 2H_2O$, in 0.05M- H_2SO_4 , whose fluorescence flux was set at 100% for $\lambda_{exc} = 350$ nm and $\lambda_{em} = 447$ nm and other instrumental parameters identical to those for measurement of the Ce(III) or Tb(III) solutions.

The fluorimetric measurements were carried out on an Aminco-Bowman J4-8961-E spectro-photofluorimeter (American Instrument Co., U.S.A.) with a 150 W xenon discharge lamp and 1 cm quartz cuvettes at 20°C. The following optimal instrumental parameters for the determination of Ce(III) in a 12M- H_3PO_4 solution were found experimentally: excitation slit 1 mm, emission slit 2 mm, cuvette space shutter completely open, photomultiplier slit 5, voltage 720 V, sensitivity 100, $\lambda_{exc} = 297$ nm, $\lambda_{em} = 346$ nm. Tb(III) was determined in 0.02–2.5M- H_2SO_4 using a wavelength of $\lambda_{exc} = 222$ nm and $\lambda_{em} = 494$ nm; the other instrumental parameters were identical with those for the determination of Ce(III).

Procedure

A known amount of standard $CeCl_3$ or $TbCl_3$ solution and other studied acids or salts was pipetted into a 25 ml volumetric flask. The mixture was filled to the mark with deionized water, tempered at 20°C and its fluorescence was measured in the cuvette space of a spectrophotofluorimeter tempered to the same temperature. The results given below are the average of three parallel measurements.

RESULTS AND DISCUSSION

Fig. 1 depicts the effect of the phosphoric acid content on the excitation and fluorescence spectra of Ce(III) solutions. As the concentration of phosphoric acid increases in the solution, the position of the first excitation maximum shifts from 256 to 250 nm and the position of the second excitation maximum from 298 to 297 nm. The fluorescence maximum shifts from 350 to 346 nm. Fig. 2 depicts the dependence of the relative fluorescence flux (measured for excitation at the first or second excitation maximum) on the H_3PO_4 concentration.

The regression dependence of the relative fluorescence flux, Φ_{rel} of a Ce(III) solution in 12M- H_3PO_4 on the Ce(III) concentration in the range from 0 to $1 \mu g ml^{-1}$ under the above optimal experimental conditions can be expressed by the straight

line

$$\Phi_{\text{rel}} = (3.37 + 0.1015 \rho_{\text{Ce}}) \%$$

$$(n = 15, s_{x,y} = 0.12, r = 0.99995) \text{ (refs}^{15,16}\text{)},$$

where ρ_{Ce} is the concentration of Ce(III) in the measured solution in ng ml^{-1} , $\Phi_{\text{rel}} = (\Phi_{\text{Ce}} S_{\text{Ce}} \cdot 100 / \Phi_{\text{quin}} S_{\text{quin}}) \%$, Φ_{Ce} is the measured fluorescence flux of Ce(III) on a microphotometer at the sensitivity switch position S_{Ce} , Φ_{quin} is the measured fluorescence flux of a standard 10^{-6}M solution of quinine sulfate at the sensitivity switch position S_{quin} (for $\lambda_{\text{exc}} = 350 \text{ nm}$, $\lambda_{\text{em}} = 447 \text{ nm}$ and the other instrumental parameters identical to those for measurements on the Ce(III) solution).

The detection limit for cerium corresponding to ten times the standard deviation of the blank¹⁶ equals 1.2 ng ml^{-1} . This is almost two orders of magnitude smaller than that given in earlier publications¹⁻⁴ on the determination of cerium in H_2SO_4 or HClO_4 at $\lambda_{\text{exc}} 255-260 \text{ nm}$ and $\lambda_{\text{em}} 350-355 \text{ nm}$. The precision of the determination of 10 ng ml^{-1} Ce(III) can be expressed in terms of the relative standard deviation, equal to 3%. No interference in the determination of $1 \mu\text{g ml}^{-1}$ cerium was observed for the following acids and metal salts up to mass ratios of $c_{\text{X}}/c_{\text{Ce}}$: 200 (HCl, H_2SO_4 , Al, Na, K, NH_4^+), 100 (Sc), 20 (Y, Th, La, Pr, Nd, Sm, Eu, Gd, Tb, Lu), 10 (HNO_3), 0.5 (Fe(III)), 0.1 (Ce(IV)).

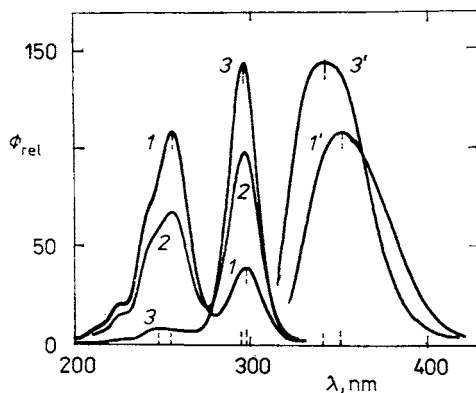


FIG. 1

The effect of phosphoric acid on the excitation and fluorescence spectra of Ce(III). Φ_{rel} relative fluorescence flux (see text); $c(\text{Ce}) = 1.3 \cdot 10^{-5} \text{ mol l}^{-1}$; curves 1-3 excitation spectra, 1', 3' fluorescence spectra; $c(\text{H}_3\text{PO}_4)$, mol l^{-1} : 1, 1' 0.03, 2 1.5, 3, 3' 12

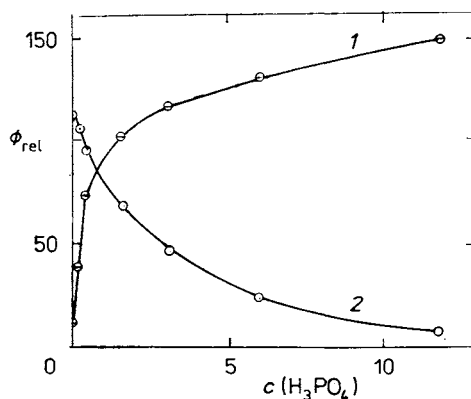


FIG. 2

The dependence of the relative fluorescence flux Φ_{rel} of a Ce(III) solution on the H_3PO_4 concentration. $c(\text{Ce}) = 1.3 \cdot 10^{-5} \text{ mol l}^{-1}$; curves: 1 $\lambda_{\text{exc}} = 256$ to 250 nm , $\lambda_{\text{em}} = 350$ to 346 nm ; 2 $\lambda_{\text{exc}} = 298$ to 297 nm , $\lambda_{\text{em}} = 350$ to 346 nm

The slope of the calibration curve is decreased and the detection limit is increased when smaller slit widths are used in the cuvette space of the spectrophotofluorimeter or photomultiplier. The fluorescence flux must then be measured at higher microphotometer sensitivities, decreasing the precision of the determination. When wider slit widths are used, the useful range of the calibration curve decreases rapidly and the detection limit increases. A decrease in the temperature to 15°C increases the fluorescence flux by about 2%, but has practically no effect on the detection limit and sensitivity of the determination.

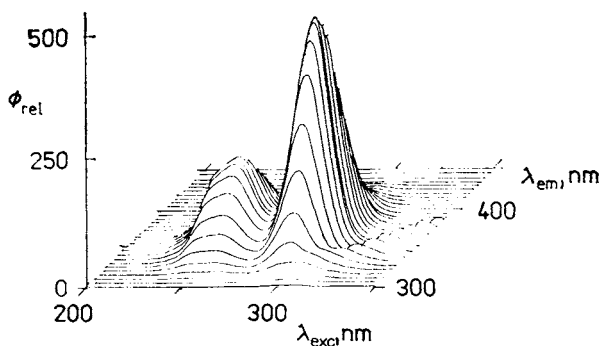


FIG. 3

Stereofluorogram of a Ce(III) solution. $c(\text{Ce}) = 2 \cdot 10^{-4} \text{ mol l}^{-1}$, $c(\text{H}_3\text{PO}_4) = 3 \text{ mol l}^{-1}$; slit widths 0.5 mm

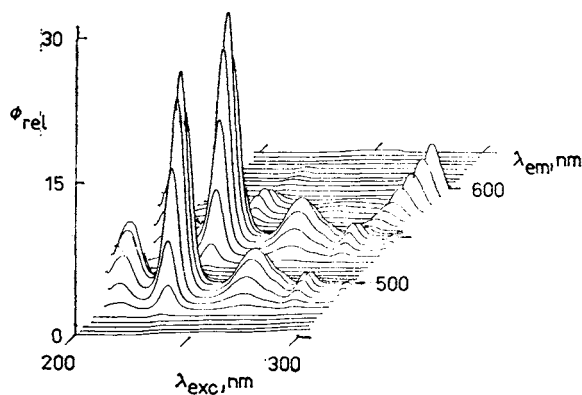


FIG. 4

Stereofluorogram of a Tb(III) solution. $c(\text{Tb}) = 2 \cdot 10^{-2} \text{ mol l}^{-1}$, $c(\text{H}_3\text{PO}_4) = 3 \text{ mol l}^{-1}$; slit widths 0.5 mm

The excitation and fluorescence spectra of Ce(III) and Tb(III) in phosphoric acid medium practically do not interact, as is apparent from the stereofluorograms in Figs 3–5. The resolution of the rather complex spectra of Tb(III) was improved by measuring the stereofluorograms at excitation and emission slit widths of 0.5 mm.

Fig. 6 depicts the spectra of Tb(III) in sulfuric acid medium under the above optimal instrumental parameters for the determination of terbium. The fluorescence

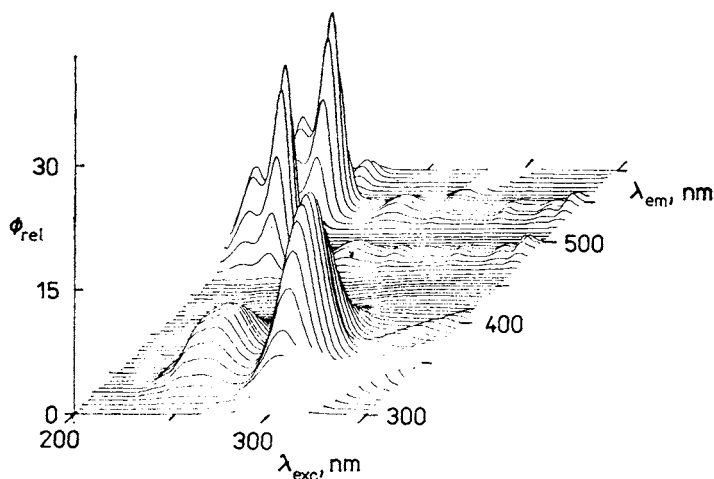


FIG. 5

Stereofluorogram of a solution of a mixture of Ce(III) and Tb(III). $c(\text{Ce}) = 1.3 \cdot 10^{-6} \text{ mol l}^{-1}$, $c(\text{Tb}) = 2 \cdot 10^{-2} \text{ mol l}^{-1}$, $c(\text{H}_3\text{PO}_4) = 3 \text{ mol l}^{-1}$; slit widths 0.5 mm

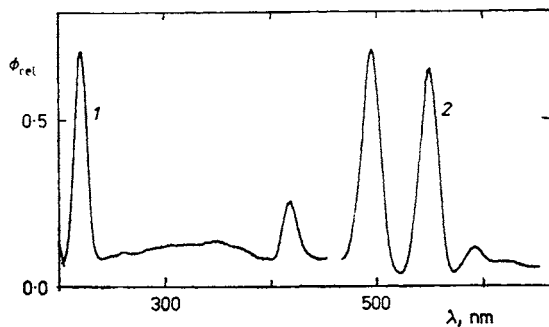


FIG. 6

Excitation and fluorescence spectra of Tb(III). Φ_{rel} relative fluorescence flux (see text); $c(\text{H}_2\text{SO}_4) = 1 \text{ mol l}^{-1}$, $c(\text{Tb}) = 2 \cdot 10^{-5} \text{ mol l}^{-1}$; curves: 1 excitation spectrum, 2 fluorescence spectrum

maximum at 494 nm is somewhat higher than the second maximum (550 nm). The regression dependence of the relative fluorescence flux of a Tb(III) solution at the first fluorescence maximum in 0.02–2.5M-H₂SO₄ on the Tb(III) concentration in the range up to 3 μg ml⁻¹ can be expressed by the straight line

$$\Phi_{rel} = (0.037 + 2.101 \cdot 10^{-4} \varrho_{Tb}) \%$$
$$(n = 15, s_{x,y} = 0.0018, r = 0.9997),$$

where ϱ_{Tb} is the concentration of terbium in the measured solution in ng ml⁻¹. The detection limit of terbium corresponding to ten times the standard deviation of the blank¹⁶ is 33 ng ml⁻¹. This is a much lower value than that published earlier on the determination of Tb in other media^{5–8}. A change in the instrumental parameters of the spectrophotometer has a similar effect on the determination of terbium as for the determination of cerium. The relative standard deviation for the determination of 50 ng ml⁻¹ Tb(III) is about 3%. No interference in the determination of 3 μg ml⁻¹ was observed for the following acids and salts up to a mass concentration ratio $c_{(X)}/c_{(Tb)}$ of: 100 (HCl), 20 (Al), 5 (Sc, Y, La, Ce(III), Pr, Nd, Sm, Eu, Gd, Lu); HNO₃, Ce(IV) and Fe(III) interfere strongly at concentrations equal to the terbium concentration. The fluorimetric determination of terbium in 0.15M-H₃PO₄ or 0.25M-HCl medium (optimal concentrations) is less sensitive than the determination in H₂SO₄ medium. The detection limits are then 40 and 60 ng ml⁻¹, respectively.

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