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Spectrophotofluorometric Determination of Terbium with α,α'-Ethylenediiminodi(*o*-hydroxyphenylacetic acid)

Tomitsugu TAKETATSU and Setsuko YOSHIDA
College of General Education, Kyushu University, Fukuoka

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Spectrophotofluorometric methods for the determination of terbium have been described using 1,10-phenanthroline–salicylic acid,[1] potassium carbonate,[2] ethylenediaminetetraacetic acid–sulfosalicylic acid,[3] 2-thenoyltrifluoroacetone,[4] and hexafluoroacetylacetone–trioctylphosphine oxide.[5] These methods are based on the measurement of luminescence, which is characteristic of the metal ion and shows the line-like spectrum, enhanced by the formation of the metal complexes. Recently we have found that the intensity of the fluorescence spectrum of terbium was remarkably enhanced by the formation of α,α'-ethylenediiminodi(*o*-hydroxyphenylacetic acid), (EDDHA), chelate. In the present paper, the fundamental conditions for the spectrophotofluorometric determination of terbium with EDDHA will be described.

Experimental

Reagents. Standard solutions of metal ions were prepared by dissolving the 99.9% pure oxides (scandium, yttrium, and the rare earths except for cerium), chlorides (cerium[III] and thorium), and nitrate (uranyl) in dilute hydrochloric acid. The concentration of scandium, yttrium, rare earth, and thorium ions were determined titrimetrically with EDTA using Xylenol Orange as an indicator. The titration of uranyl ion with EDTA was made using PAN as an indicator.

Standard solution of EDDHA was prepared by dissolving the known amount of the reagent obtained from the Dojindo Co., Ltd. Research laboratories in dilute sodium hydroxide solution.

All other chemicals used were analytical reagent grade.

Apparatus. Fluorometric measurement was carried out using a Hitachi fluorescence spectrophotometer Model 203 with a medium pressure mercury lamp. 1 cm × 1 cm quartz cell was used.

Procedure. A dilute hydrochloric acid solution containing less than about 50 μg was transferred into a beaker. Then, 5 m*l* of 2.5×10^{-3} M EDDHA solution and 2 m*l* of 5% triethanolamine solution were added to the solution. After the pH of the solution was adjusted to 7.6—7.8 with dilute hydrochloric acid and sodium hydroxide solutions, the solution was transferred into a 25 m*l* volumetric flask and made up to volume with water. The intensity of the fluorescence of the solution was measured on the spectrophotofluorometer. The apparent excitation and fluorescence wavelengths used were 295 and 545 nm, respectively. The content of terbium was calculated by using the calibration curve obtained from the standard. A solution of quinine sulfate was used to a constant reading for measurement made at 545 nm.

Results and Discussion

Fluorescence Spectrum. The apparent fluorescence spectrum of the solution (pH 7.7), containing the terbium-EDDHA chelate, excited with radiation at a wavelength of 295 nm is shown in Fig. 1. The apparent wavelengths of the prominent maxima of the fluorescence spectrum are 487, 545, and 585 nm and the most intense wavelength is 545 nm.

Effect of pH. Figure 2 shows the variation of the fluorescence at 545 nm as a function of pH. The apparent fluorescence gives almost constant over pH range 7.5—7.8. In this case, triethanolamine was used as the buffer reagent because it gave an effective buffer action in the pH region from 6.5 to 8 and the intensity of fluorescence was not influenced by an addition of excessive amounts of the reagent.

Effect of EDDHA Concentration. The variation of intensity of the fluorescence was investigated as a function of mole ratio (EDDHA/Tb^{3+}) plots. The intensity of the fluorescence gives almost constant over

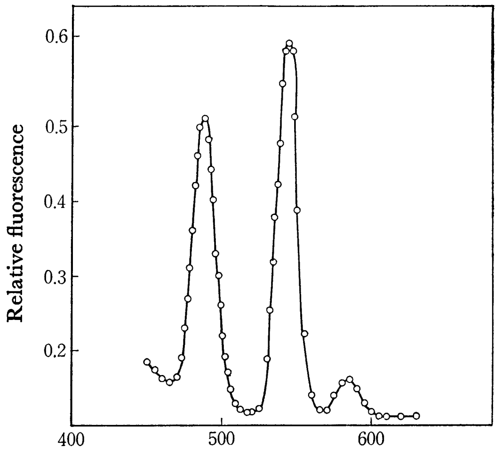

Fig. 1. Apparent fluorescence spectrum of terbium-EDDHA complex.
1.0×10^{-5} M Tb^{3+}, 5.0×10^{-4} M EDDHA, pH 7.7, excitation wavelength 295 nm.

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[3] R. M. Dagnall, R. Smith, and T. S. West, *Analyst* (London), **92**, 358 (1967).

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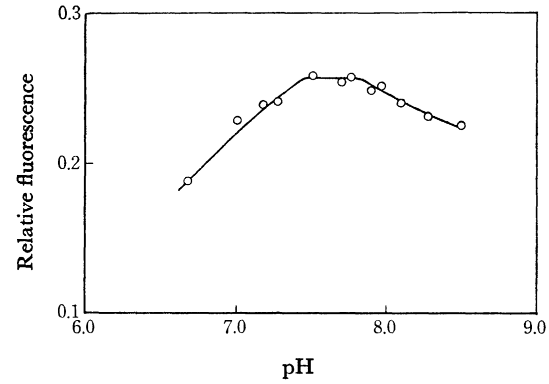

Fig. 2. Variation of intensity of the fluorescence as a function of pH.
1.0×10^{-6} M Tb^{3+}, 1.0×10^{-4} M EDDHA, excitation wavelength 295 nm, fluorescence wavelength 545 nm.

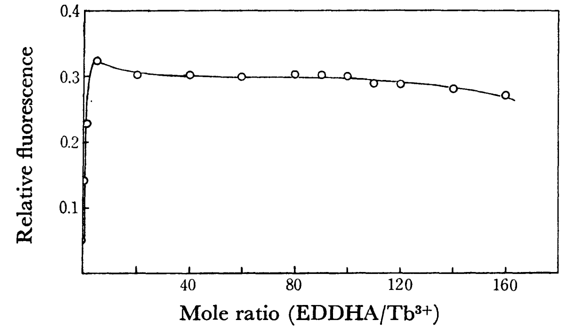

Fig. 3. Variation of intensity of the fluorescence as a function of concentration of EDDHA.
5.0×10^{-6} M Tb^{3+}, pH 7.7, excitation wavelength 295 nm, fluorescence wavelength 545 nm.

the mole ratio range 20—100 as shown in Fig. 3.

Stability of Fluorescence with Time. The intensity of the fluorescence remained sensibly constant for 7 hr after a few minutes.

Calibration Experiments. It is found that the fluorescence is a linear function of the concentration in the range from 0.03 to 1.5 μg/m*l* of terbium as shown in Fig. 4. Also, by amplifying the sensitivity of the instrument, the linear relationship is obtained for solutions containing from 0.0015 to 0.015 μg/m*l*.

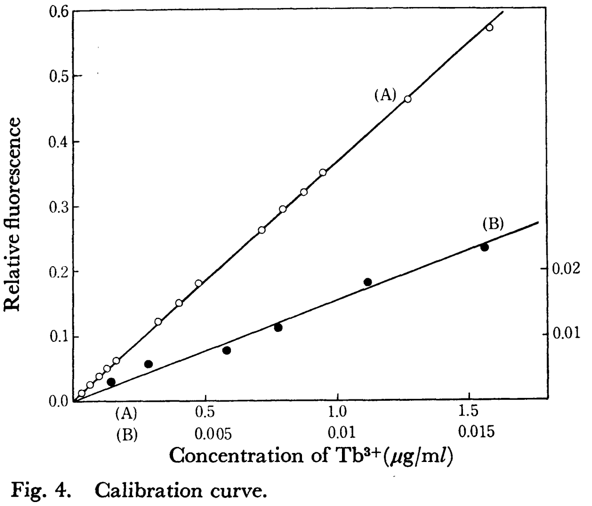

Fig. 4. Calibration curve.
(A) 1.0×10^{-4} M EDDHA: (B) 1.0×10^{-5} M EDDHA, pH 7.7 excitation wavelength 295 nm, fluorescence wavelength 545 nm. Relative fluorescence between (A) and (B) does not represent the correlative intensity.

TABLE 1. DETERMINATION OF TERBIUM IN SYNTHETIC SAMPLES CONTAINING DIVERSE METAL IONS

Metal ions added, μg		Tb[a)] found, μg	Metal ions added, μg		Tb[a)] found, μg
La	50.0	19.3	Ho	32.9	18.7
Ce	22.7	17.9	Ho	61.4	19.3
Ce	45.2	17.4	Er	32.9	19.1
Pr	22.1	19.0	Er	61.5	19.9
Pr	44.4	18.6	Tm	25.3	19.7
Nd	24.2	18.5	Tm	50.7	21.0
Nd	48.5	18.3	Yb	28.3	19.3
Sm	23.9	18.6	Yb	59.7	20.1
Sm	47.7	18.4	Lu	27.3	19.9
Eu	24.9	18.8	Y	32.2	19.6
Eu	49.8	18.8	Sc	7.8	19.4
Gd	23.6	19.0	UO_2	42.8	19.4
Gd	47.2	19.2	Th	33.7	13.6
Dy	47.9	19.9	Th	67.3	11.3

a) *Tb taken, 19.9 μg

Effect of Other Substances. The effect of other rare earth, scandium, yttrium, thorium, and uranyl ions was studied under the optimum conditions. The results are shown in Table 1. Lanthanum, gadolinium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, scandium, yttrium, and uranyl ions do not interfere. Cerium, praseodymium, neodymium, samarium, and europium give a slight interference. Thorium gives a serious interference.

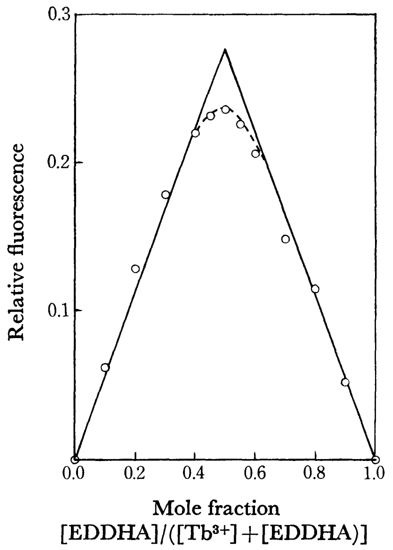

Fig. 5. Continuous variation plot.
$[Tb^{3+}]+[EDDHA]=1.0\times10^{-5}$ M, pH 7.7, excitation wavelength 295 nm, fluorescence wavelength 545 nm.

Composition of the Terbium-EDDHA Chelate. The continuous variation method was used to investigate the ratio in which EDDHA combines with terbium. The total concentration of EDDHA and terbium was maintained at 1.0×10^{-5}M. The continuous variation plot is illustrated in Fig. 5. The peak at mole fraction

Table 2. A comparison amoung data found in various literatures.

Reagents	Range of linearity or limit of detection	Condition of experiment	Literatures
1,10-Phenanthroline-salicylic acid	0.05 μg/ml	in benzene (solvent extraction)	1)
Potassium carbonate	0.3—70 μg/ml	in 1.5 M K_2CO_3 solution	2)
Ethylenediaminetetraacetic acid–sulfosalicylic acid	0.0064—3.2 μg/ml	in alkaline solution at pH 11.6—11.9	3)
2-Thenolytrifluoroacetone	10^{-3} to 10 M 0.15—15 μg/ml	in dimethylformamide	4)
Hexafluoroacetylacetone–trioctylphosphine oxide	10^{-7} to 10^{-4} M 0.015—15 μg/ml	in methylcyclohexane (solvent extraction)	5)
EDDHA	0.03—1.5 g/ml and 0.0015—0.015 μg/ml	in weak alkaline solution at pH 7.5—7.8	This paper

[EDDHA]/([EDDHA]+[Tb^{3+}]) of 0.5 indicates combining ratio of one EDDHA molecule per one terbium ion.

Comparison with Other Methods. Table 2 shows a comparison amoung the data reported by several investigators. The EDDHA method can be carried out more easily and rapidly in comparison with the methods[1,5] which are in need of solvent extraction procedure. Also it is known that the present method is almost similar to or superior to the other methods concerning the range of linearity and the degree of limit of detection though the comparison is not always appropriate because the data depend upon the performance of instruments used.