

Fluorometric Determination of Europium with Benzoyltrifluoroacetone

Tsunenobu SHIGEMATSU, Masakazu MATSUI
and Takayuki SUMIDA.*

Received September 16, 1968

Determination of traces of europium as benzoyltrifluoroacetone chelate was studied. Trioctylphosphine oxide adduct of the chelate, which has a fluorescence maximum at 612 $m\mu$, was formed in *n*-hexane solution by utilizing synergistic effect in solvent extraction. The effect of various factors on the fluorescence intensity at 612 $m\mu$ was examined. This method enabled us to detect europium in a concentration as low as 2×10^{-8} M (or 3.04×10^{-2} μg per 10 ml). Of the other rare earth ions, only samarium gave a positive error. Other common di- and trivalent cations had little effect except ferric ion which caused a negative error.

I. INTRODUCTION

Recently many works have been done on the spectrofluorometric determination of rare earth ions because of its high sensitivity and selectivity. The simultaneous determination of dysprosium, europium, samarium and terbium was investigated in 0.6M sodium tungstate solution.¹⁾ Europium and terbium were determined fluorometrically in a *o*-phenanthroline-salicylic acid system, by the extraction of them into benzene.²⁾ These methods are interfered by some of the other rare earth ions. Taketatsu *et al.*³⁾ have investigated the fluorometric analysis of terbium and europium in potassium carbonate solution. Dagnall, Smith and West⁴⁾ examined EDTA-sulphosalicylic acid system and made a specific determination of terbium in the concentration ranging from 6.4×10^{-3} to 3.2 μg of terbium per ml. McCarthy and Wineforder⁵⁾ studied the possibilities of determining dysprosium, europium, samarium and terbium fluorometrically in nonaqueous solutions of aromatic carbonyl compounds.

Some β -diketone chelates of europium are also known to fluoresce⁶⁻⁹⁾. They have attracted attention as possible laser materials. These compounds have strong and broad absorption bands in the near ultraviolet which were caused by the $\pi \sim \pi^*$ transition of their benzenoid ring. Their fluorescence gives a relatively sharp line characteristic of the metal ion. This phenomenon based on the intramolecular energy transfer was tried to apply for the specific and sensitive determination of europium in the present paper.

Kononenko *et al.*¹⁰⁾ investigated the fluorometry of europium and samarium in *o*-phenanthroline thenoyltrifluoroacetone system, Ballard and Edwards¹¹⁾ that of europium in TTA-trioctylphosphate system and Stanley *et al.*¹²⁾ that of europium, samarium, terbium and gadolinium using TTA, benzoylacetone and dibenzoylmethane by computer spectrum stripping techniques.

The fluorescence intensity of β -diketone chelates in the solvent extraction

* 重松恒信, 松井正和, 角田孝之: Laboratory of Radiochemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

method decreases rapidly as the ligand concentration increases because of the emission based on the intramolecular energy transfer. In the present work, the authors examined the fluorometric determination of europium as benzoyltrifluoroacetone-(BFA)-trioctylphosphine oxide (TOPO) complex by using the synergistic effect in solvent extraction.¹³⁾

II. EXPERIMENTALS

Reagents.

A $2 \times 10^{-3} M$ stock solution of europium was prepared by dissolving 0.0352 g europium oxide (Shin-Etsu Chem. Ind. Co., Ltd. 99.9 per cent Eu_2O_3) with concentrated hydrochloric acid, by evaporating to dryness and by diluting to 100 ml with redistilled water. The other rare earth solutions were prepared in a manner similar to the europium solution from their oxides of 99.99 per cent in purity.

Benzoyltrifluoroacetone and trioctylphosphine oxide (Dojindo & Co., Ltd, Research Laboratory) were used without further purification. *n*-Hexane, purified by the bistillation, was used as the solvent for the extraction of the chelates.

Rhodamine B was used as an internal standard. The other chemicals were reagent grade materials.

Apparatus.

A Hitachi spectrophotometer, Model EPU-2 equipped with an attachment for fluorescence measurement was used for obtaining spectra and intensity. A mercury arc was used as light source and the fused silica cell of 10 mm in light path as sample container. The pH measurements were performed with a Hitachi-Horiba Model M-4 pH meter.

Procedure.

An aliquot of a solution containing over 0.03 μg of europium and 1 ml of buffered solution (1.0 M NaAc-HAc) were taken into a 20 ml beaker. The pH of the solution was then adjusted to the desired value by the addition of 1 M hydrochloric acid or 1 M sodium hydroxide. The aqueous phase was transferred into a 25 ml separating funnel and finally diluted to 10 ml with water. After 10 ml of *n*-hexane solution consisting of $5 \times 10^{-4} M$ BFA and $2 \times 10^{-2} M$ TOPO was added, the funnel was shaken for 30 min., and allowed to settle. The organic phase was carefully separated through a filter paper. The fluorescence intensity was measured at 612 $m\mu$ against a 0.3 μg per ml of rhodamine B as an internal standard, by using an excitation wavelength of 365 $m\mu$.

III. RESULTS AND DISCUSSION

Fluorescence Spectrum.

The fluorescence spectrum for the *n*-hexane solution of europium-BFA-TOPO system containing $1.0 \times 10^{-6} M$ of europium, $5 \times 10^{-4} M$ of BFA and $2 \times 10^{-2} M$ of TOPO, respectively, is shown in Fig. 1. The spectrum has a maximum peak at 612 $m\mu$, which is characteristic of europium ion. Three tenth microgramme per ml of rhodamine B was used as an internal standard, and *n*-hexane was chosen as an extractant solvent, because it has no absorbance in near ultraviolet region. The fluorescence intensity was measured throughout the experiment at 612 $m\mu$.

Effect of pH.

To establish the optimum pH value of the aqueous phase for the fluorometry

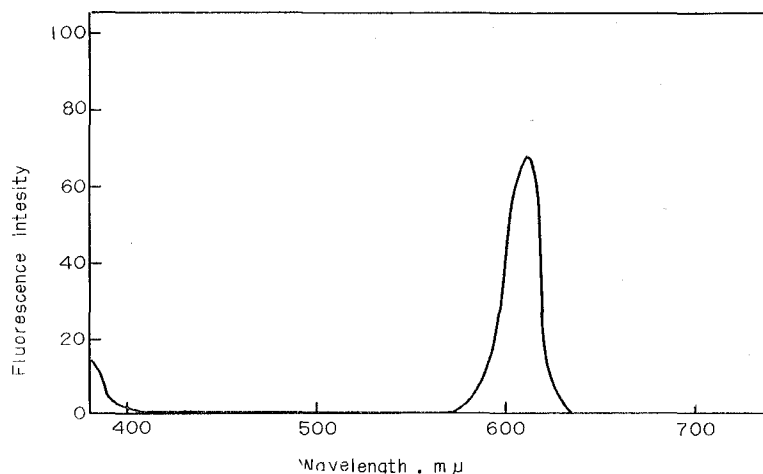


Fig. 1. Fluorescence spectrum of europium BFA adduct.
Eu: $1 \times 10^{-6} M$, BFA: $5 \times 10^{-4} M$, TOPO: $2 \times 10^{-2} M$

of europium, the dependence of the fluorescence intensity on the pH value was investigated. In Fig. 2 the fluorescence intensity is shown as a function of pH for the three systems:

System I: Eu $5 \times 10^{-7} M$, BFA $5 \times 10^{-4} M$, TOPO $2 \times 10^{-2} M$

System II: Eu $1 \times 10^{-5} M$, BFA $1 \times 10^{-2} M$, TOPO $1 \times 10^{-2} M$

System III: Eu $1 \times 10^{-6} M$, BFA $1 \times 10^{-3} M$, TOPO $1 \times 10^{-2} M$

It is seen from the figure that nearly constant intensities are obtained through a considerably wide range of pH (pH value from 3 to 5.5) for all the systems. Taking this result into account, the pH value was kept at 4.50 throughout the following experiments.

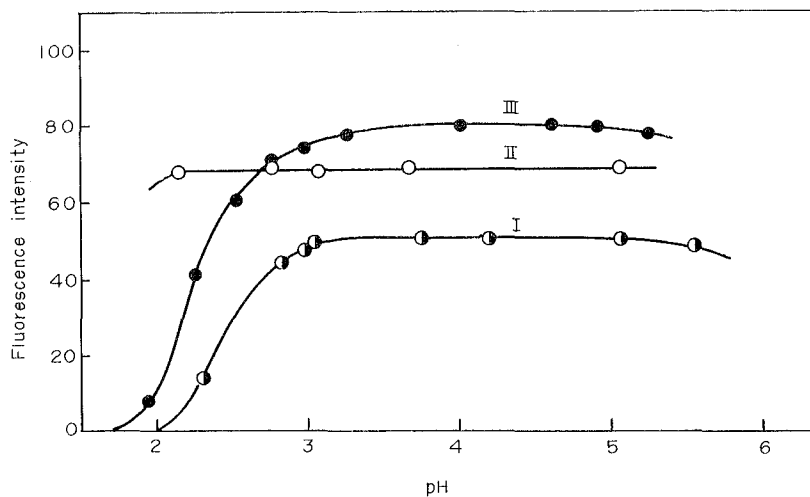


Fig. 2. Effect of pH on fluorescence intensity.
I: Eu $5 \times 10^{-7} M$, BFA $5 \times 10^{-4} M$, TOPO $2 \times 10^{-2} M$
II: Eu $1 \times 10^{-5} M$, BFA $1 \times 10^{-2} M$, TOPO $1 \times 10^{-2} M$
III: Eu $1 \times 10^{-6} M$, BFA $1 \times 10^{-3} M$, TOPO $1 \times 10^{-2} M$

Effect of TOPO Concentration.

In the solvent extraction, some metal chelates can be often extracted at a lower pH region by adding such Lewis bases as trioctylphosphine oxide. If this phenomenon, generally called synergistic effect, can be applied to the present system, the chelates could be extracted quantitatively even at the considerably low concentration of the chelating agent. This would be useful for the sensitive fluorometry of the element. Then, the effect of TOPO concentration on the fluorescence intensity was examined. As shown in Fig. 3, a nearly constant intensity was obtained when the concentration of TOPO was over $2 \times 10^{-4} M$. The authors used $2 \times 10^{-2} M$ of TOPO was used in all other experiments.

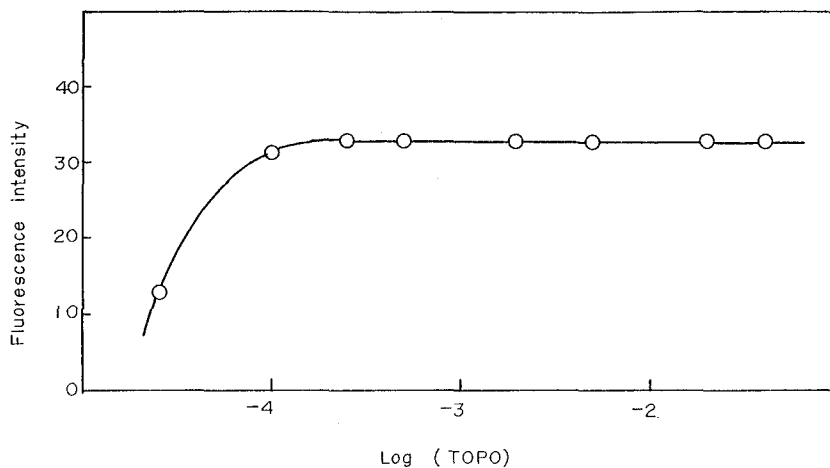


Fig. 3. Effect of TOPO concentration.
Eu: $5 \times 10^{-7} M$, BFA: $5 \times 10^{-4} M$

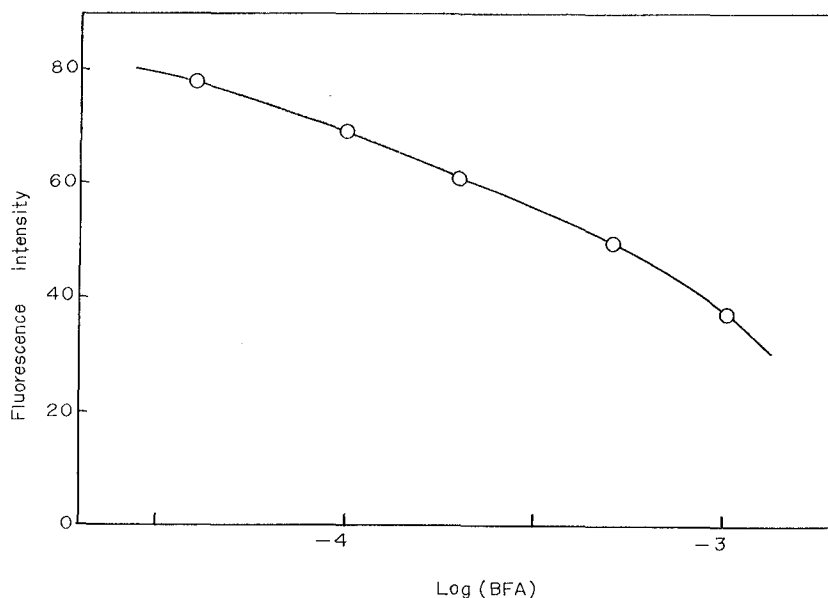


Fig. 4. Effect of the concentration of the chelating agent.
Eu: $5 \times 10^{-7} M$, TOPO: $2 \times 10^{-2} M$

Effect of the Concentration of the Chelating Agent.

After the europium chelate ($5 \times 10^{-7} M$) was extracted at pH 4.5 with the chelating agent of various concentrations, the fluorescence intensity was measured at 612 $m\mu$. The intensity decreased rapidly in inverse proportion to the reagent concentration in the range between 10^{-2} and $10^{-3} M$. This is because of the fluorescence caused by the intramolecular energy transfer as described above. As the reagent concentration became further low, the reagent effect on the intensity slightly softened, as shown in Fig. 4. In consideration of sensitivity and practical use, $5 \times 10^{-4} M$ of BFA was used throughout the other experiments.

Effect of Temperature.

The fluorescence intensity was measured at various temperatures. As shown in Fig. 5, the intensity decreased gradually as the temperature was raised. The decrease in the intensity was 0.55 per cent degree.

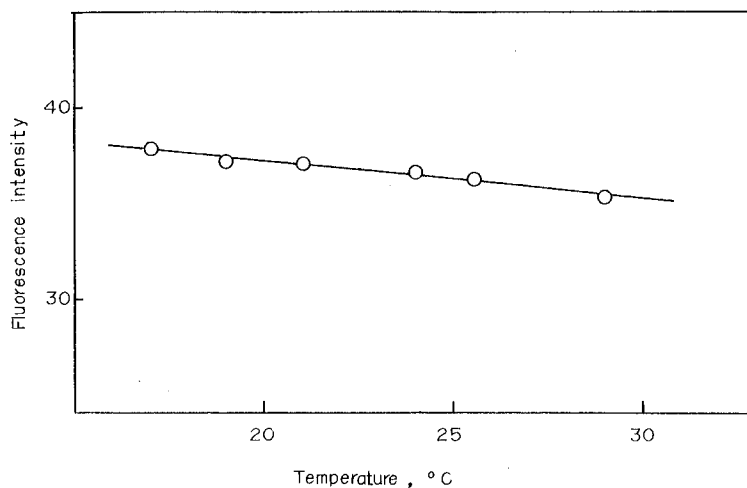


Fig. 5. Effect of temperature.
Eu: $5 \times 10^{-7} M$, BFA: $5 \times 10^{-4} M$, TOPO: $2 \times 10^{-2} M$

Effect of Standing and Shaking Time.

The intensity of the *n*-hexane solution of europium-BFA-TOPO chelate was measured at 612 $m\mu$ at appropriate intervals of time to examine the effect of the standing and shaking time. As shown in Fig. 6, little influence of the standing and shaking time was observed upon the intensity of the organic phase for 10 min. and over.

Calibration Curves.

A calibration curve was made by extracting a different amount of europium into 10 ml portion of *n*-hexane solution containing $5 \times 10^{-4} M$ of BFA and $2 \times 10^{-2} M$ of TOPO from 10 ml portion of aqueous solution at pH 4.50. The fluorescence intensity was measured at 612 $m\mu$ against 0.3 μg per ml of rhodamine B as an internal standard. A good linear relationship was obtained by plotting the intensity of the organic phase against the concentration of europium added in the aqueous solution, as shown by curve I in Fig. 7. The other curve in the figure (curve II) was made by extracting the aqueous solution into *n*-hexane solution containing $5 \times 10^{-5} M$ of BFA and $2 \times 10^{-2} M$ of TOPO and by measuring the intensity under the most sensitive condition

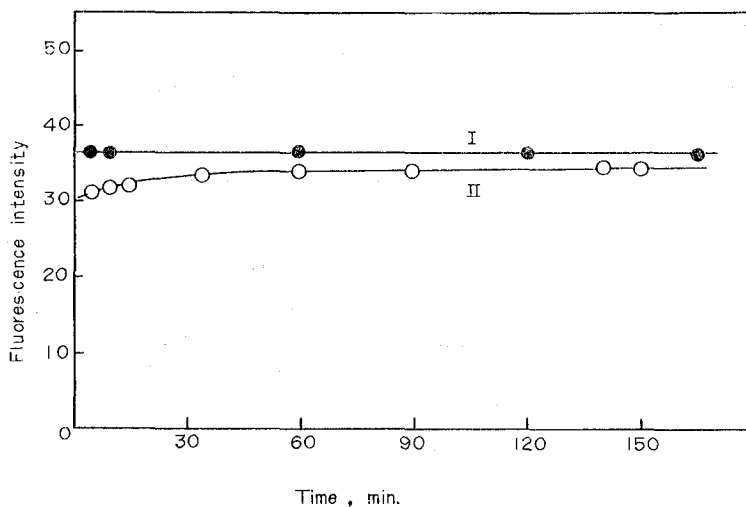


Fig. 6. Effect of shaking and standing time.
I: shaking time, II: standing time

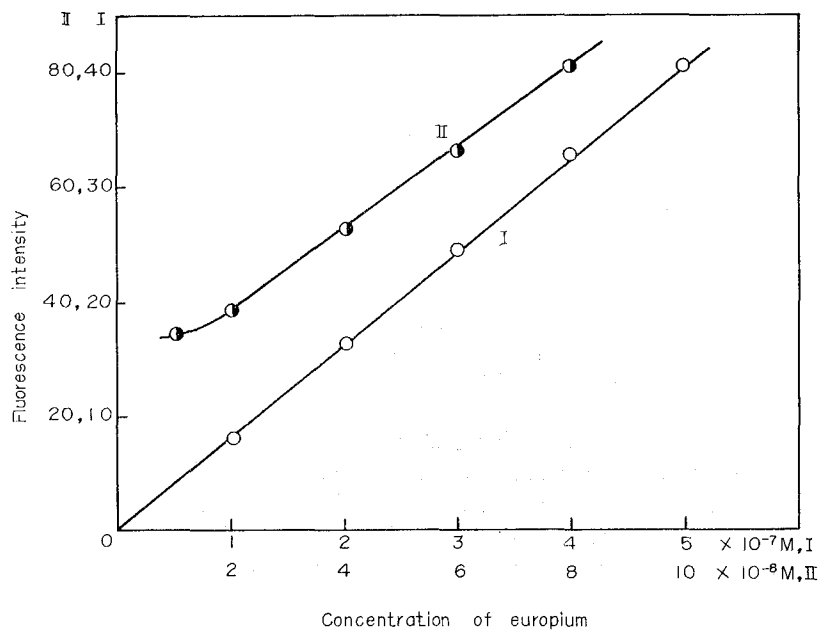


Fig. 7. Calibration curves of europium.
I: BFA $5 \times 10^{-4} M$, TOPO $2 \times 10^{-2} M$
II: BFA $5 \times 10^{-5} M$, TOPO $2 \times 10^{-2} M$

of the present instrument. The curve shows that $2 \times 10^{-8} M$ of europium ($3.04 \times 10^{-2} \mu g$ per 10 ml) was detectable in the present method.

Effect of Diverse Ions.

The effect of diverse ions was examined with the solution containing $10.76 \mu g$ of europium and various diverse ions. The pH value of the aqueous phase was adjusted at pH 4.50. Of the other rare earth ions tested, only samarium gave a

positive error, while common di- and trivalent cations had little effect on the fluorescence intensity except iron (III) which caused a negative error, as shown in Table I.

Table I. Effect of co-existing ions
Europium taken, 0.76 μg .

Ion	Added, μg	Eu found, μg	Ion	Added, μg	Eu found, μg
Y ³⁺	5	,73	Fe ³⁺	4	,72
La ³⁺	5	,72		10	,64
Pr ³⁺	5	,74	Cu ²⁺	4	,78
Nd ³⁺	5	,78	Ni ²⁺	25	,77
Sm ³⁺	20	,86	In ³⁺	10	,78
Gd ³⁺	10	,72	Co ²⁺	100	,76
Tb ³⁺	5	,73	Cr ³⁺	500	,76
Dy ³⁺	10	,76	V ⁵⁺	500	,77
Ho ³⁺	10	,73	Mn ²⁺	500	,77
Er ³⁺	10	,76	Cd ²⁺	500	,80
Tm ³⁺	10	,75	Mo ⁶⁺	500	,76
Yb ³⁺	10	,76	Al ³⁺	400	,80
Lu ³⁺	10	,77	Bi ³⁺	500	,78
Ce ³⁺	5	,75	Pb ²⁺	500	,79
Sc ³⁺	4	,76	Mg ²⁺	400	,80
Hf ⁴⁺	10	,78	Ca ²⁺	400	,80
Zr ⁴⁺	10	,78	Sr ²⁺	500	,78
U ⁶⁺	5	,76	Ba ²⁺	400	,78
Zn ²⁺	30	,75	Sb ³⁺	1000	,80

REFERENCES

- (1) G. Alberti and M. A. Massucci, *Anal. Chem.*, **34**, 214 (1966).
- (2) L. I. Kononenko, R. S. Lauer and N. S. Poluektov, *Zh. Analit. Khim.*, **18**, 1468 (1963).
- (3) T. Taketatsu, M. A. Carey and C. V. Banks, *Talanta*, **13**, 1081 (1966)
- (4) R. M. Dagnall, R. Smith and T. S. West, *Analyst*, **92**, 358 (1967)
- (5) W. J. McCarthy and J. D. Winefordner, *Anal. Chem.*, **38**, 849 (1966).
- (6) G. A. Crosby, R. E. Whan and R. M. Aline, *J. Chem. Phys.*, **34**, 743 (1961).
- (7) H. Winston, O. J. Marsh, C. K. Suzuki and C. L. Telk, *ibid* **39**, 267 (1963).
- (8) F. Halverson, J. S. Brinen and J. R. Leto, *ibid* **41**, 157 (1964).
- (9) N. Filipescu, W. F. Sager and F. A. Serafin, *J. Phys. Chem.*, **68**, 3324 (1964).
- (10) L. I. Kononenko, N. S. Poluektov and M. P. Nikonova, *Zav. Lab.*, **30**, 779 (1964).
- (11) R. E. Ballard and J. W. Edwards, *Anal. Abstr.*, 3466 (1966).
- (12) E. C. Stanley, B. I. Kinneberg and L. P. Varga, *Anal. Chem.*, **38**, 1362 (1966).
- (13) T. Shigematsu, M. Tabushi, M. Matsui and T. Honjyo, *Bull. Chem. Soc. Japan*, **40**, 2807 (1967).