

Flow Injection Analysis of Samarium(III) and  
Europium(III) Based on Solubilizing the Ternary  
Complexes with Thenoyltrifluoroacetone and  
Trioctylphosphine Oxide in Micellar Solution

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ABSTRACT

Complex formation of samarium(III) and europium(III) with thenoyltrifluoroacetone(TTA) and trioctylphosphine oxide(TOPO) in micellar solution has been studied by flow injection analysis/stopped flow method. The presence of TOPO was found to access the complex formation. A flow injection spectrofluorimetric method has been developed for the determination of samarium(III) as its ternary complex with TTA and TOPO in a micellar solution of nonaoxyethylenedodecyl ether (BE-9EX).

## INTRODUCTION

Taketatsu et al. found that europium(III), samarium(III) and terbium(III) ternary complexes with  $\beta$ -diketone in the presence of TOPO are readily soluble in an aqueous solution containing non-ionic surfactant and that the strong fluorescence originating from the ternary complexes can be applied to the determination of lanthanide ions.<sup>1-3</sup> We have reported flow injection spectrofluorimetric determination of europium(III) and terbium(III) based on solubilizing the ternary complexes in micellar solution.<sup>4,5</sup>

In this paper, the formation of samarium(III) and europium(III) complexes with thenoyltrifluoroacetone and trioctylphosphine oxide in a micellar solution of BL-9EX was investigated by the flow injection analysis/ stopped-flow method and the determination of samarium (III) was studied by the flow injection analysis.

## EXPERIMENTAL

Stock solutions of mixed ligands(TTA and TOPO) were prepared by dissolving the reagents(Dojindo Laboratories) in an aqueous solution of non-ionic surfactant. The surfactants used were BL-9EX(Nikko

Chemical Co. LTD.), Emulgen 120(Kao-Atlas Co. LTD.) and Triton X100(Wako Pure Chemical Ind. LTD.).

The flow injection system is shown in Fig. 1. Detector was a spectrofluorimeter(UVIDIC-610, Japanspectroscopic Co.) with a flow cell(32  $\mu$ l)

Sample containing samarium(III) at concentrations in range  $10^{-6}$  -  $10^{-5}$  M(0.15 - 1.5  $\mu$ g/ml) were injected into the system at rate of 60 samples per hour. The fluorescence was measured at apparent excitation and emission wave lengths of 355 and 596 nm, respectively.

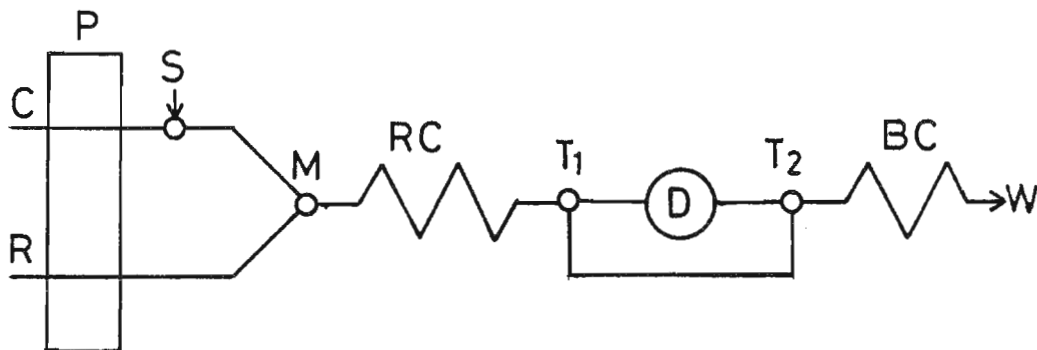
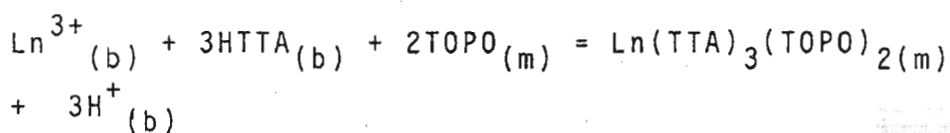


Fig. 1. Flow manifold. C, 0.5 % BL-9EX and acetate buffer solution; R, TTA-TOPO, 0.5 % BL-9EX and buffer solution; S, sample injection(100 $\mu$ l); M, mixing joint; RC, reaction coil; T<sub>1</sub>, stopped-flow valve; T<sub>2</sub>, three way joint; D, detector; BC, back pressure coil(1m); P, pump and W, waste.

For the stopped-flow method, the switching valve was switched to lead the carrier solution to waste(W) and to stop the sample zone in the flow cell.

## RESULTS AND DISCUSSION

The following equilibrium for lanthanide(III)-TTA-TOPO system was postulated in a micellar solution<sup>1-3</sup>.



where Ln is lanthanide(III) ion and the subscripts(b) and (m) refer to mutually equilibrated bulk and micellar phases, respectively.

The effect of different surfactants on the stopped flow pattern of these systems was investigated and periods required for complex formation were determined. The kind of non-ionic surfactants essentially does not influence the complex formation. Fig.2 and Fig.3 show typical examples of reaction curves for Sm(III)-TTA, TTA-TOPO and Eu(III)-TTA, TTA-TOPO systems at various pH. The periods required for the formation of the complexes are given in Table 1. The presence of TOPO was found to access the formation of complex. The intensity for both systems gave constant over the pH range of 3 - 5. The pH of 3.5 was selected because of the prevent of hydrolysis of lanthanide(III) ion.

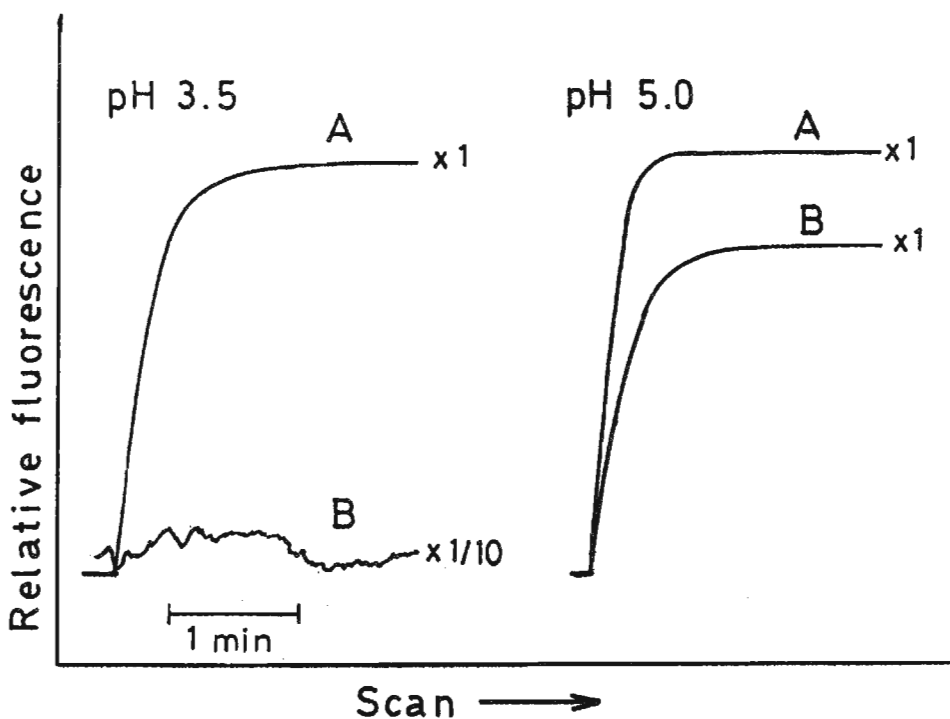


Fig. 2. Stopped-flow signals obtained with the flow system.  $[\text{Sm(III)}] = 2 \times 10^{-5}$  M. A,  $[\text{TTA}] = [\text{TOPO}] = 4 \times 10^{-4}$  M; B,  $[\text{TTA}] = 4 \times 10^{-4}$  M.

Table 1. Periods required for formation of samarium(III) and europium(III) complexes

pH	Sm(III) complexes		Eu(III) complexes	
	TTA	TTA-TOPO	TTA	TTA-TOPO
	sec	sec	sec	sec
3.5	---	47.5	---	39.5
5.0	77.0	35.0	107.5	33.0

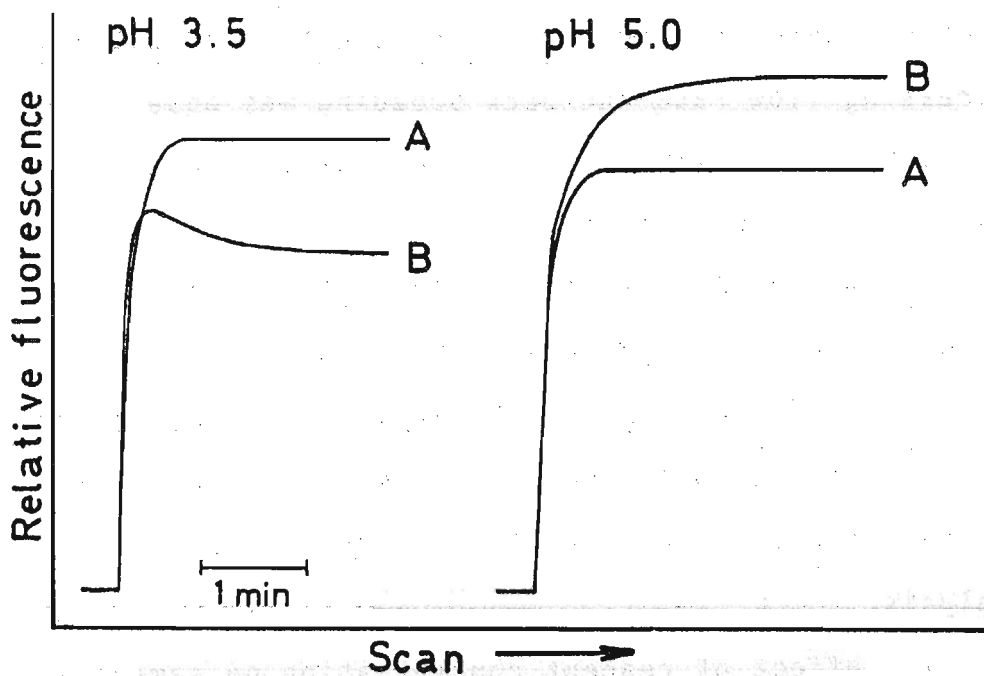


Fig. 3. Stopped-flow signals obtained with the flow system.  $[\text{Eu(III)}] = 2 \times 10^{-5} \text{ M}$ .

#### Chemical and Flow Injection Variable

##### Effect of BL-9EX concentration

The effect of BL-9EX concentration on samarium(III) ternary complex formation with TTA and TOPO were studied. The peak height decreased as the BL-9EX concentration increased. A concentration of 0.5% was chosen for subsequent work.

##### Effect of flow rate, coil length and reagent concentration

The flow rates of the reagent and the carrier

solutions were studied. The peak height increased with increasing flow rate and peak broadening was observed from 0.8 to 1.0 ml/min. The flow rate of 1.0 ml/min. was chosen for subsequent work.

The effect of reaction coil length was tested by use of 0.5 - 3 m length while the flow rate was maintained at 1.0 ml/min. The peak heights decreased with increasing coil length. A 1 m coil length was chosen because of the sensitivity and the rapid analysis.

The effect of reagent concentration on samarium (III) emission as its ternary complex with TTA and TOPO was studied. The peak height increased as the mixed reagent concentration increased. The constant peak height was obtained at  $3 - 4 \times 10^{-4}$  M. A mixed reagent concentration of  $4 \times 10^{-4}$  M for TTA and TOPO was chosen for subsequent work.

#### Determination of samarium(III) ion

Samples containing  $10^{-6}$  -  $10^{-5}$  M samarium(0.15 - 1.5  $\mu\text{g/ml}$ ) were injected into the carrier stream under the flowing optimum condition; Concentration of TTA and TOPO  $4 \times 10^{-4}$  M; concentration of BL-9EX 0.5 w/v %, pH 3.5 ; flow rate 1 ml/min., coil length, 1m(0.5mm id.). Typical calibration peaks are shown in Fig 4. The

calibration graphs obtained were linear in the range  $10^{-6}$  -  $10^{-5}$  M. The precision of the method was checked on ten samples containing  $4 \times 10^{-6}$  M samarium(III). The relative standard deviation was less than 4.0 %.

### Interferences

The influence of other rare earth ions on the determination  $1.20 \mu\text{g/ml}$  was studied. The results are given in Table 2. It was found that equi amount of La etc. had no significant effect.

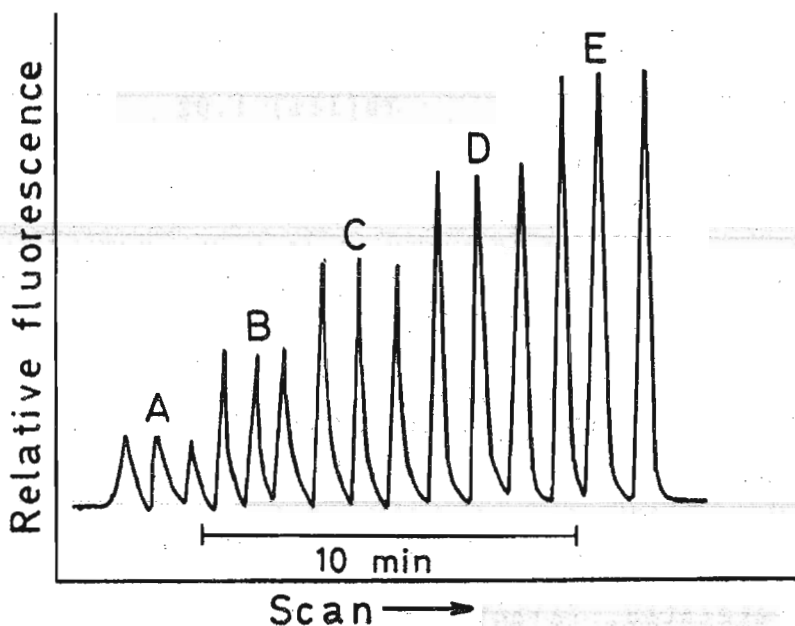


Fig. 4. Peaks obtained for triplicate injections of standard Sm(III) solution.  $[\text{Sm(III)}]$  : A,  $2 \times 10^{-6}$  M; B,  $4 \times 10^{-6}$  M; C,  $6 \times 10^{-6}$  M; D,  $8 \times 10^{-6}$  M; E,  $10 \times 10^{-6}$  M.



Table 2. Effect of other ions on determination of samarium(III). Sm(III) taken, 1.20 µg/ml

Ion added	Sm(III) found µg/ml	Recovery %	Ion added	Sm(III) found µg/ml	Recovery %
La(III)	1.24	103	Ho(III)	1.22	101
Ce(IV)	1.21	100	Er(III)	1.16	96
Pr(III)	1.16	96	Tm(III)	1.19	99
Nd(III)	1.15	96	Dy(III)	1.18	98
Gd(III)	1.17	97	Yb(III)	1.02	85
Tb(III)	1.21	100	Lu(III)	1.24	103

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