# CHAPTER 3

# DETERMINATION OF EUROPIUM WITH CHLORTETRACYCLINE AS A COMPLEXING AGENT

## 3.1 Introduction

As previously mentioned in Chapter 1, there are several methods for determining europium in a variety of matrices namely spectrofluorimetric [62], polarographic [65] and voltammetric [66] procedures. However, all these procedures are troublesome or the instruments are not readily available. Therefore, there is the need for suitable laboratories equipped with inexpensive instrumentation, which allows the determination of europium to be carried out in a fast and cheap way without sacrificing precision. Flow injection spectrophotometric method is a method that satisfies these requirements and can be afforded by most laboratories.

In this research work, chlortetracycline (CTC), an important member of the tetracycline group of antibiotics, has been used as a complexing agent for determining trace amount of europium(III). The chemical structure of CTC is shown in Figure 3.1.

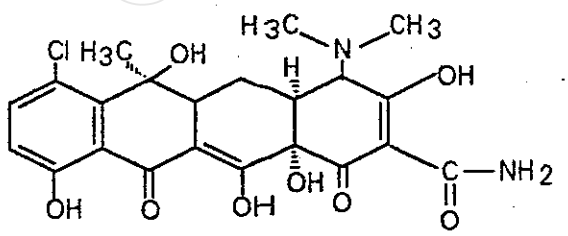


**Figure 3.1** : Chemical structure of CTC [74].

## 3.2 Experimental

### 3.2.1 Apparatus and Instruments

1. UV-VIS spectrophotometer model UV - 265, Shimadzu, Kyoto, Japan.
2. CECIL 1000 SERIES, Cecil Instruments, Cambridge, England.
3. Spectronic 21, Milton Roy Company, USA.
4. Recorder, Servograph REC 51, Radiometer Copenhegen, Denmark.
5. Flow-through cell for spectrophotometer, Hellma, Germany.
6. Home-made injection valve [75].
7. Peristaltic pump EYELA SMP-23S, Tokyo Rikakikai Co., Ltd., Japan.
8. pH/mV meter model 5986-2S, Cole - Parmer, Co., Ltd., USA.
9. Tygon plastic tube (I.D. 0.030, 0.0402, 0.0449, and 0.060 in).
10. Teflon tube (I.D. 0.050 in).
11. Test tube (O.D. 1.20, 1.60 1.80, and 2.40 in).
12. Disposable syringe (1 ml), Nissho Nipro Corporation Ltd., Thailand.

### 3.2.2 Chemicals

1. Europium(III) chloride hexahydrate ($EuCl_3.6H_2O$), A.R. grade, Fluka, Switzerland.
2. Tris(hydroxymethyl) aminomethane ($C_4H_{11}NO_3$), Fluka, Switzerland.
3. Hydrochloric acid (HCl) , 36.5-38.0%, A.R. grade, J.T. Baker Inc., Phillipsberg, USA.
4. Chlortetracycline hydrochloride (CTC.HCl), Fluka, Switzerland.

### 3.2.3 Preparation of Standard Solutions and Reagents

(1) Standard europium(III) solution (100 ppm)

A stock solution of europium(III) was made by dissolving 0.2417 g of europium(III) chloride hexahydrate ($EuCl_3.6H_2O$) in deionized water and diluted in a 1 l volumetric flask. Solutions of lower concentration were obtained by accurate dilution of this solution.

(2) Standard CTC solution ($1.0 \times 10^{-3}$ M)

This standard solution of chlortetracycline was prepared by dissolving 0.0479 g of its hydrochloride salt into a 100 ml volumetetric flask and making up to volume with deionized water. Working standard solutions were then prepared daily by successive dilution of the stock standard solution.

(3) Tris - buffer solution pH 8.0

This buffer was prepared by dissolving 1.21 g of tris(hydroxymethyl) aminomethane in 1 l of deionized water and adjusting the pH to 8.0 with 1 M hydrochloric acid.

### 3.2.4 Manifold and Procedure

A two - line manifold was designed as shown in Figure 3.2 and used for all flow injection runs. A 100 µl sample loop was used for injecting the sample into the merged streams of CTC reagent and the buffer solution streams which were pumped at the same flow rate (3.0 ml/min). Europium(III) formed the Eu(III) - CTC complex and the absorbance was monitored at 400 nm. The experimental set - up of the FI system for Eu(III) determination was shown in Figure 3.3.

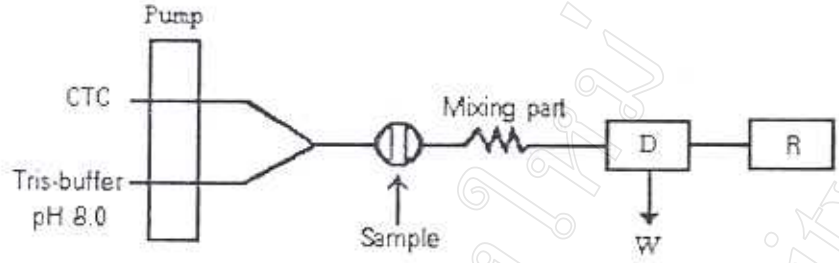


Figure 3.2 : FIA manifold for Eu(III) determination with CTC.

Figure 3.3 : FIA system for Eu(III) determination with CTC.

1. Reagent reservoir
2. Buffer reservoir
3. Peristaltic pump
4. Injection valve
5. Mixing part
6. Flow-through cell
7. Detector
8. Recorder
9. Waste

## 3.3 Results and Discussion

### 3.3.1 Preliminary Studies of the Complex

#### 3.3.1.1 Absorption Spectra of CTC and Europium(III) - CTC Complex

The absorption spectra of CTC and Eu(III) - CTC complex were scanned between 300 - 500 nm (Figure 3.4). The yellow solution of CTC showed a maximum absorption at 368 nm while the complex having a maximum absorption at 400 nm. This corresponds to that previously reported by Hirschy et. al. [77].

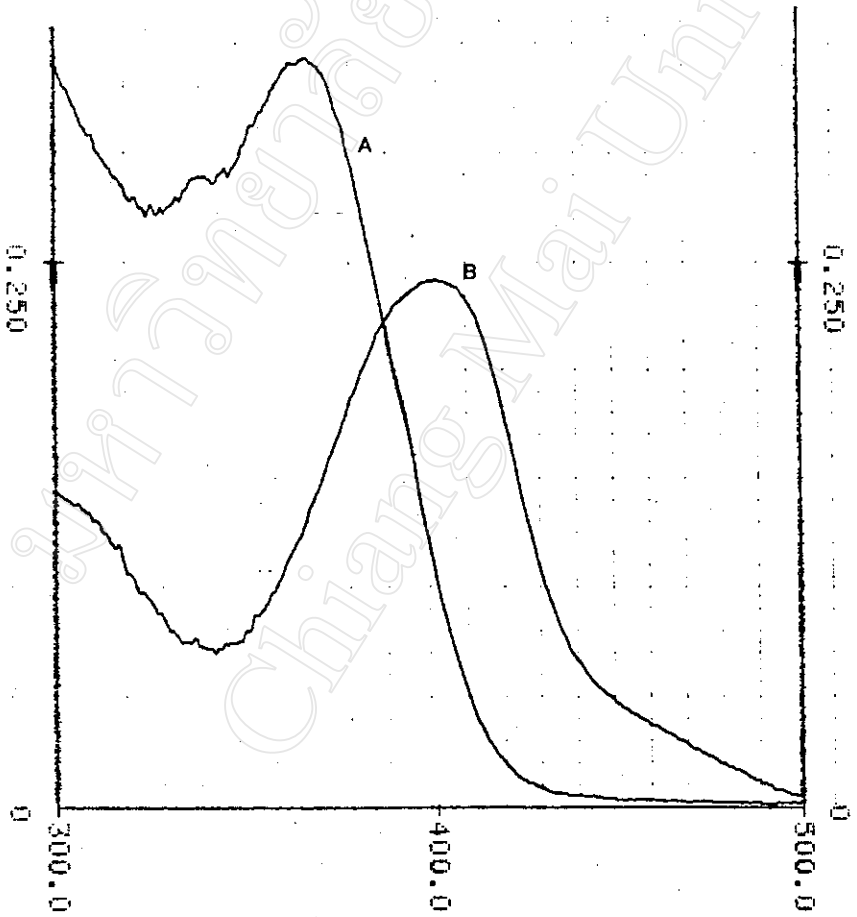


**Figure 3.4 :** Absorption spectra of A, CTC, and B, the Eu(III) - CTC complex.

### 3.3.1.2 Composition of the Eu(III) - CTC Complex

A study of the composition of the Eu(III) - CTC complex using the continuous variations and mole ratio method indicated that the complex has a 1:1 composition (see Figure 3.5). The results of these studies were shown in Table 3.1.

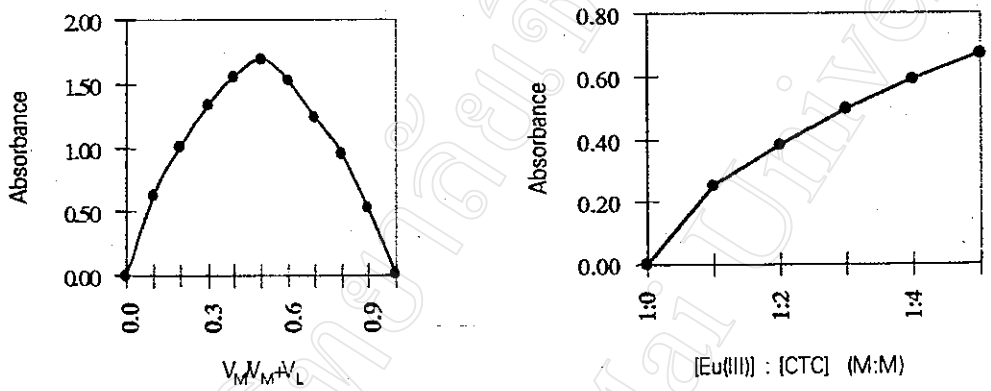


**Figure 3.5** : Determination of the composition of Eu(III) - CTC complex by (a) continuous variations, and (b) mole ratio method.

**Table 3.1 :** The absorbance of Eu(III) - CTC complexes.

| Continuous variations method | | Mole ratio method | |
|---|---|---|---|
| $V_M / V_M+V_L$ | Absorbance | Mole Eu / CTC | Absorbance |
| 0 | 0.008 | 1 : 0 | 0.000 |
| 0.10 | 0.629 | 1 : 1 | 0.250 |
| 0.20 | 1.003 | 1 : 2 | 0.380 |
| 0.30 | 1.335 | 1 : 3 | 0.493 |
| 0.40 | 1.550 | 1 : 4 | 0.587 |
| 0.50 | 1.682 | 1 : 5 | 0.669 |
| 0.60 | 1.529 | | |
| 0.70 | 1.241 | | |
| 0.80 | 0.954 | | |
| 0.90 | 0.527 | | |
| 1.00 | 0.015 | | |

### 3.3.2 Optimization of the Flow System

#### 3.3.2.1 Effect of various wavelengths on peak height

This was investigated by injecting the standard europium(III) solution into the carrier stream with the fixed analytical parameters by random as shown in Table 3.2. The results in Table 3.3 and Figure 3.6 shows that the optimum wavelength chosen is 400 nm, since it provides reproducible results with a high sensitivity.

**Table 3.2** : The fixed analytical parameters by random for europium(III) determination with CTC at varying wavelengths (380 - 440 nm).

| Analytical Characteristics | Information |
|---|---|
| conditions of the FI system | |
| conc. of CTC (M) | $1.25 \times 10^{-4}$ |
| conc. of Eu(III) (ppm) | 1.0 |
| injection volume (μl) | 100 |
| pH | 7.5 |
| flow rate of Eu(III) solution (ml/min) | 4.5 |
| flow rate of tris - buffer pH 7.5 (ml/min) | 4.5 |
| inner diameter of mixing tubing (in) | 0.0402 |
| length of mixing tubing (m) | 1.00 |
| shape of mixing part | coil |
| conditions of detector | |
| absorbance range | 0 - 2 |
| conditions of recorder | |
| chart speed (min/cm) | 5 |
| sensitivity (mV/cm) | 20 |

**Table 3.3 :** Effect of operating wavelength on peak height from 100 ng Eu(III).

| Wavelength (nm) | Peak height * | |
|---|---|---|
| | cm | mV |
| 380 | 0.60 | 12.00 |
| 385 | 0.50 | 10.00 |
| 390 | 0.65 | 13.00 |
| 395 | 1.07 | 21.40 |
| 400 | 3.25 | 65.00 |
| 405 | 3.00 | 60.00 |
| 410 | 2.50 | 50.00 |
| 415 | 2.02 | 40.40 |
| 420 | 1.63 | 32.60 |
| 425 | 1.22 | 24.40 |
| 430 | 0.92 | 18.40 |
| 435 | 0.63 | 12.60 |
| 440 | 0.40 | 8.00 |

* average of triplicate results.

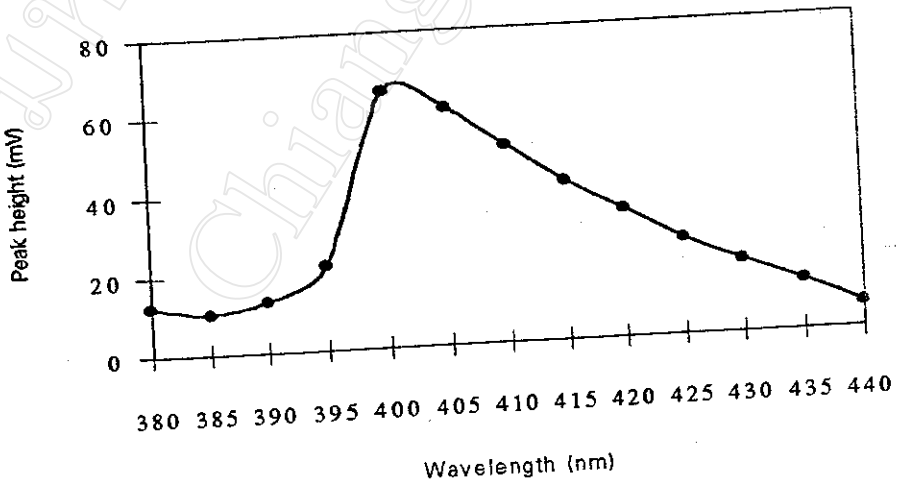


**Figure 3.6 :** Relationship between peak height (mV) from 100 ng Eu(III) with various wavelengths.

### 3.3.2.2 Effect of pH

The effect of pH on the peak heights from various concentrations of Eu(III) (1.0 - 5.0 ppm) was studied by varying the pH of tris-buffer from 7.0 to 9.0. The results in Table 3.4 and Figure 3.7 showed that the best sensitivity was obtained when the pH of tris - buffer was adjusted to 8.0.

**Table 3.4 :** Effect of pH on peak height.

| pH / Eu(III) (ppm) | Peak height (mV)* | | | | |
|---|---|---|---|---|---|
| | 7.0 | 7.5 | 8.0 | 8.5 | 9.0 |
| 1.0 | 2.00 | 7.00 | 6.60 | 4.80 | 6.40 |
| 2.0 | 5.00 | 10.60 | 11.80 | 9.40 | 11.00 |
| 3.0 | 7.00 | 14.20 | 16.60 | 14.00 | 13.00 |
| 4.0 | 10.00 | 17.00 | 21.40 | 18.60 | 20.00 |
| 5.0 | 12.00 | 12.00 | 26.00 | 20.60 | 20.00 |
| Slope (mV/ppm) | 2.50 | 3.36 | 4.84 | 4.08 | 4.28 |
| Correlation coefficient | 0.9976 | 0.9983 | 0.9998 | 0.9920 | 0.9772 |

* average of triplicate results.

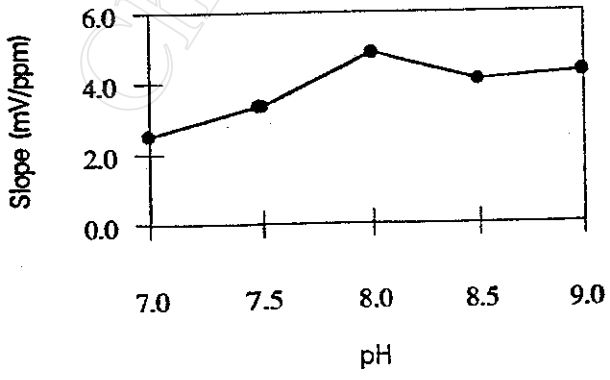


**Figure 3.7 :** Relationship between slope (mV/ppm) and pH of tris - buffer.

### 3.3.2.3 Effect of CTC concentration

This was investigated by varying the concentration of CTC solution ranging from $1.0 \times 10^{-5}$ to $1.0 \times 10^{-4}$ M. The results obtained are shown in Table 3.5 and Figure 3.8. From the experimental results, $4.0 \times 10^{-5}$ M CTC solution was chosen as optimum concentration for subsequent experiments.

**Table 3.5 :** Effect of CTC concentration on peak heights.

| [CTC], M / Eu(III) (ppm) | Peak height (mV)* | | | | |
|---|---|---|---|---|---|
| | $1.0 \times 10^{-5}$ | $2.0 \times 10^{-5}$ | $4.0 \times 10^{-5}$ | $5.0 \times 10^{-5}$ | $1.0 \times 10^{-4}$ |
| 1.0 | 8.00 | 8.80 | 8.00 | 5.40 | 14.60 |
| 2.0 | 10.00 | 13.00 | 12.40 | 14.40 | 18.00 |
| 3.0 | 10.40 | 14.00 | 17.00 | 18.00 | 23.00 |
| 4.0 | 10.40 | 15.60 | 22.40 | 22.40 | 30.00 |
| 5.0 | 10.00 | 18.00 | 25.40 | 26.00 | 29.40 |
| Slope (mV/ppm) | 1.20 | 2.10 | 4.48 | 4.92 | 5.12 |
| Correlation coefficient | 0.9332 | 0.9736 | 0.9971 | 0.9797 | 0.9878 |
| $t_{base}$ (sec) | 48 | 54 | 54 | 60 | 96 |
| Sample/hr | 75 | 67 | 67 | 60 | 37 |

* average of triplicate results.

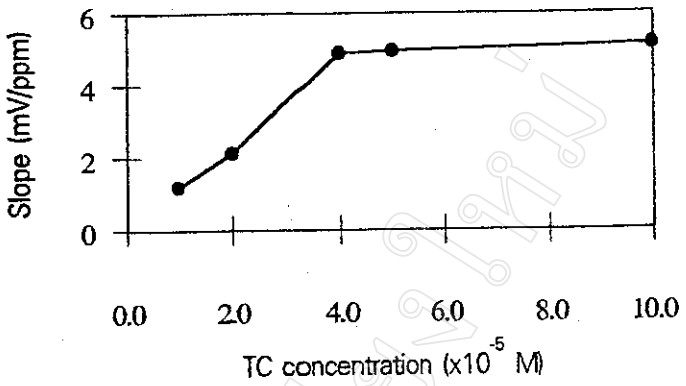


**Figure 3.8 :** Relationship between slope (mV/ppm) and CTC concentration (M).

### 3.3.2.4 Effect of flow rate

This was investigated by injecting 100 µl of standard europium solution containing 1.0 - 5.0 ppm of Eu(III) into the FIA system. A 4.0 x $10^{-5}$ M CTC solution was used as carrier. Different flow rates ranging from 2.0 to 4.0 ml/min were studied. The results were summarized in Table 3.6 and Figure 3.9. The results indicated that a flow rate of 3.0 ml/min was chosen as optimum because it provided the highest sensitivity and the better linearity of standard calibration curve.

Table 3.6 : Effect of carrier flow rate on peak height.

| Carrier flow rate (ml/min) / Eu(III) (ppm) | Peak height (mV)* | | | | |
|---|---|---|---|---|---|
| | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 |
| 1.0 | 3.40 | 7.40 | 8.20 | 13.00 | 8.60 |
| 2.0 | 9.00 | 12.40 | 13.60 | 19.00 | 16.60 |
| 3.0 | 11.40 | 20.60 | 18.20 | 23.40 | 20.60 |
| 4.0 | 13.60 | 23.00 | 23.20 | 25.40 | 22.60 |
| 5.0 | 15.40 | 23.00 | 28.40 | 26.60 | 25.40 |
| Slope (mV/ppm) | 2.86 | 4.18 | 5.47 | 3.36 | 3.96 |
| Correlation coefficient | 0.9692 | 0.9396 | 0.9997 | 0.9568 | 0.9601 |
| $t_{base}$ (sec) | 90 | 84 | 57 | 57 | 54 |
| Sample/hr | 40 | 43 | 63 | 63 | 67 |

* average of triplicate results.

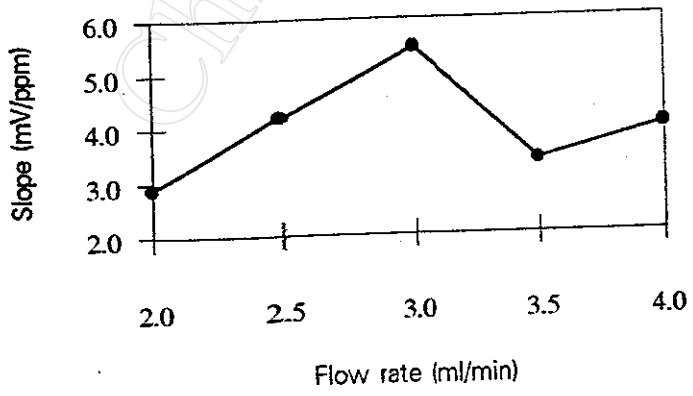


Figure 3.9 : Relationship between slope (mV/ppm) and carrier flow rate (ml/min).

### 3.3.2.5 Effect of inner diameter of mixing tubing

This effect was studied by injecting 100 µl of the standard europium(III) solution (1.0 - 5.0 ppm) into the carrier stream. Mixing coils with different inner diameters, viz: 0.030", 0.0402", 0.0449" and 0.060" were evaluated and compared. The resulting experimental observations were summarized in Table 3.7. As regards to sensitivity, a suitably high sensitivity combined with a suitably short $t_{base}$ (and, hence, a high sample throughput) was obtained with an inner diameter of 0.0449". This inner diameter of mixing tubing was therefore taken as the optimum value for subsequent analyses.

**Table 3.7 :** Effect of the inner diameters of mixing tubing on peak height.

| I.D. of mixing tubing (in) / Eu(III) (ppm) | Peak height (mV)* | | | |
|---|---|---|---|---|
| | 0.030 | 0.0402 | 0.0449 | 0.060 |
| 1.0 | 6.00 | 21.40 | 20.60 | 12.40 |
| 2.0 | 10.00 | 32.40 | 32.60 | 19.20 |
| 3.0 | 12.00 | 38.60 | 40.00 | 23.60 |
| 4.0 | 14.00 | 40.00 | 43.60 | 27.40 |
| 5.0 | 15.40 | 40.00 | 48.00 | 30.40 |
| Slope (mV/ppm) | 2.28 | 6.20 | 6.58 | 4.42 |
| Correlation coefficient | 0.9793 | 0.9450 | 0.9682 | 0.9872 |
| $t_{base}$ (sec) | 96 | 96 | 60 | 60 |
| Sample/hr | 37 | 37 | 60 | 60 |

* average of triplicate results.

### 3.3.2.6 Effect of mixing tubing length

In order to achieve maximum sensitivity and the sampling rate, the effect of mixing tubing length was also studied by varying the tube length of mixing part from 25 to 100 cm. The results are summarized in Table 3.8 and Figure 3.10. A mixing tubing length of 75 cm was chosen as optimum length.

**Table 3.8 :** Effect of mixing tubing length on peak height.

| Length (cm) / Eu(III) (ppm) | Peak height (mV)* | | | |
|---|---|---|---|---|
| | 25 | 50 | 75 | 100 |
| 1.0 | 6.00 | 6.00 | 2.80 | 7.40 |
| 2.0 | 14.60 | 11.60 | 10.00 | 16.00 |
| 3.0 | 20.20 | 19.60 | 19.60 | 22.00 |
| 4.0 | 26.00 | 25.40 | 28.00 | 27.40 |
| 5.0 | 28.00 | 31.60 | 32.00 | 31.00 |
| Slope (mV/ppm) | 5.54 | 6.50 | 7.64 | 5.86 |
| Correlation coefficient | 0.9797 | 0.9986 | 0.9926 | 0.9882 |
| $t_{base}$ (sec) | 63.0 | 66.0 | 54.0 | 60.0 |
| Sample/hr | 57 | 54 | 67 | 60 |

* average of triplicate results.

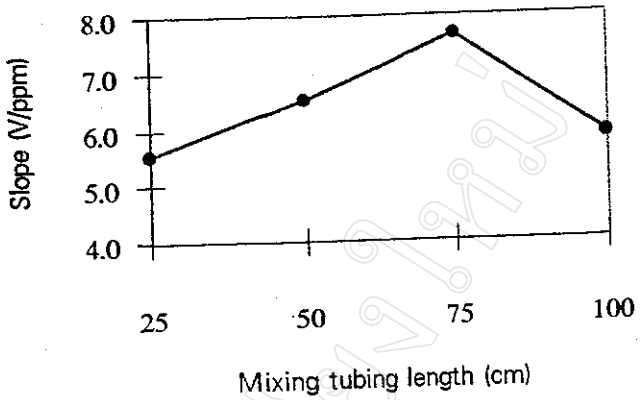


**Figure 3.10 :** Relationship between slope (mV/ppm) and mixing tubing length (cm).

### 3.3.2.7 Effect of using a glass bead columns as a mixing reactor

The effect of using a glass bead column or single bead string reactor (s.b.s.r.) as a mixing reactor was studied by varying length of s.b.s.r. reactor from 3.0 to 11.0 cm. A glass bead column used in this investigation was made from silicone tubing 3.2 mm I.D., and packed with glass beads (3.0 mm diameter in single straight line). The conditions were varied in similar manner as previously described. The results were shown in Table 3.9 and Figure 3.11. The good sensitivity (regards as slope in mV/ppm) and sample throughput were obtained when the glass bead column length was 5.0 cm.

**Table 3.9 :** Effect of glass bead column length on peak height.

| Length (cm) / Eu(III) (ppm) | Peak height (mV)* | | | | |
|---|---|---|---|---|---|
| | 3.0 | 5.0 | 7.0 | 9.0 | 11.0 |
| 1.0 | 34.00 | 28.00 | 23.00 | 29.60 | 24.00 |
| 2.0 | 36.00 | 29.40 | 29.40 | 35.40 | 29.40 |
| 3.0 | 40.60 | 37.40 | 35.60 | 42.00 | 34.00 |
| 4.0 | 45.40 | 42.00 | 37.40 | 44.60 | 36.40 |
| 5.0 | 48.00 | 44.60 | 37.40 | 46.60 | 36.00 |
| Slope (mV/ppm) | 3.74 | 4.58 | 4.94 | 4.32 | 4.18 |
| Correlation coefficient | 0.9914 | 0.9785 | 0.9756 | 0.9723 | 0.9868 |
| $t_{base}$ (sec) | 54 | 48 | 60 | 66 | 72 |
| Sample/hr | 66 | 75 | 60 | 54 | 50 |

* average of triplicate results.

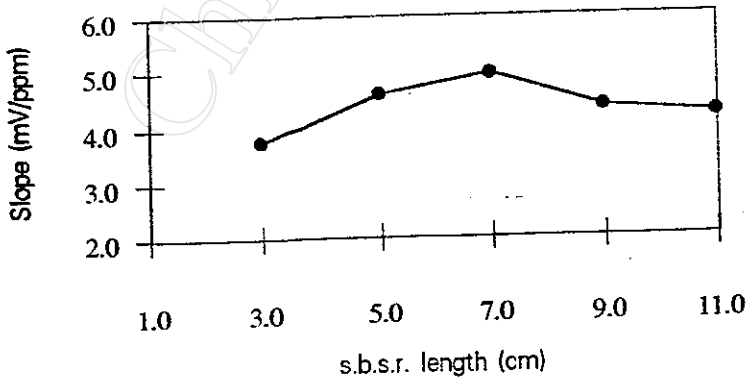


**Figure 3.11 :** Relationship between slope (mV/ppm) and s.b.s.r length (cm).

### 3.3.2.8 Effect of various mixing reactor types

The effect of varying the mixing reactor types (zigzag 1 cm x 1 cm, zigzag 1.5 cm x 1.5 cm, coil, knitted, straight line, s.b.s.r.) was tested under similar conditions as previously described. The results were shown in Table 3.10 and Figure 3.12.

From Table 3.10 and Figure 3.12, the results shown that the use of s.b.s.r. as a mixing reactor of the FIA system should be satisfactory because it provided a suitably high sensitivity combined with a suitably short $t_{base}$ and sample throughput.

**Table 3.10 :** Effect of mixing reactors on peak height.

| Reactor type / Eu(III) (ppm) | Peak height (mV)* | | | | | |
|---|---|---|---|---|---|---|
| | Zigzag 1 x 1 | Zigzag 1.5 x 1.5 | coil | knitted | straight line | s.b.s.r. |
| 1.0 | 6.60 | 14.40 | 17.40 | 24.00 | 17.20 | 17.00 |
| 2.0 | 8.00 | 20.80 | 25.00 | 31.00 | 23.60 | 23.20 |
| 3.0 | 13.60 | 25.40 | 30.40 | 38.60 | 28.00 | 29.60 |
| 4.0 | 14.60 | 29.40 | 33.40 | 36.00 | 35.40 | 35.20 |
| 5.0 | 19.40 | 32.00 | 35.00 | 38.00 | 39.60 | 41.60 |
| Slope (mV/ppm) | 3.22 | 4.36 | 4.36 | 3.30 | 5.66 | 6.12 |
| Correlation coefficient | 0.9786 | 0.9684 | 0.9630 | 0.8549 | 0.9968 | 0.9997 |
| $t_{base}$ (sec) | 48 | 54 | 48 | 48 | 42 | 42 |
| Sample/hr | 75 | 66 | 75 | 75 | 85 | 85 |

* average of triplicate results.

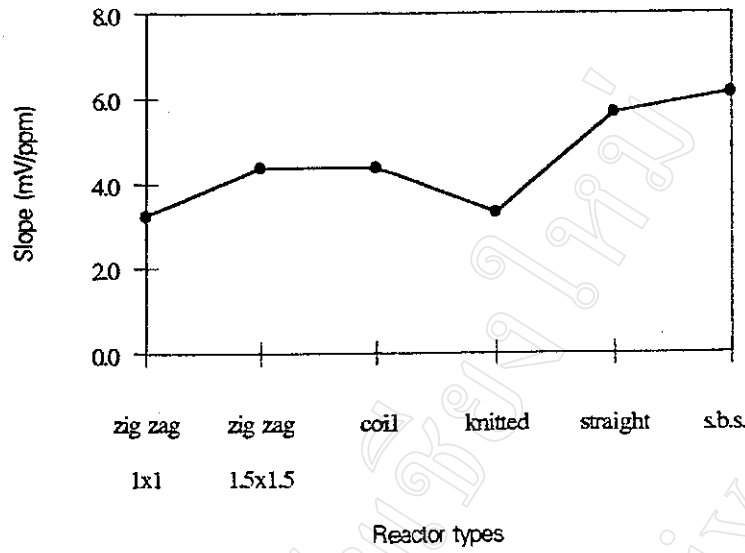


**Figure 3.12 :** Relationship between slope (mV/ppm) and reactor types.

### 3.3.2.9 Effect of injection volume

The effect of injection volume was investigated by varying a loop length of injection valve. In this research work, this effect was investigated from 50 to 200 µl. The results were shown in Table 3.11 and Figure 3.13. A volume of 100 µl was chosen as a compromise between good sensitivity and a sampling frequency of samples per hour.

**Table 3.11 :** Effect of the injection volume on peak height.

| Reagent volume (µl) / Eu(III) (ppm) | Peak height (mV)* | | | |
|---|---|---|---|---|
| | 50 | 100 | 150 | 200 |
| 1.0 | 14.40 | 12.60 | 11.60 | 16.60 |
| 2.0 | 18.00 | 18.40 | 20.60 | 18.00 |
| 3.0 | 21.40 | 26.00 | 26.00 | 20.00 |
| 4.0 | 23.40 | 30.00 | 26.60 | 23.40 |
| 5.0 | 26.00 | 33.00 | 30.60 | 28.60 |
| Slope (mV/ppm) | 2.86 | 5.24 | 4.40 | 2.94 |
| Correlation coefficient | 0.9937 | 0.9862 | 0.9480 | 0.9673 |
| $t_{base}$ (sec) | 42 | 54 | 54 | 41 |
| Sample/hr | 85 | 66 | 66 | 87 |

* average of triplicate results.

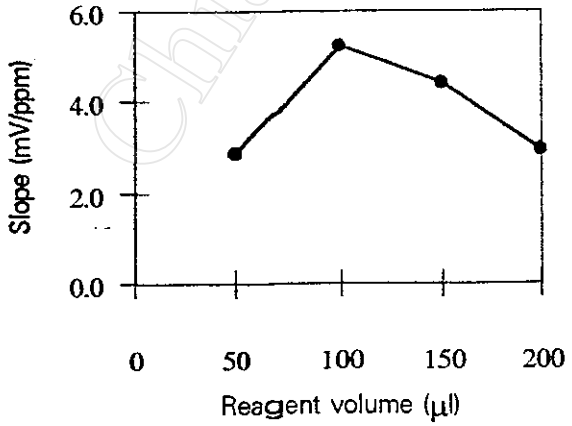


**Figure 3.13 :** Relationship between slope (mV/ppm) and injection volume (µl).

### 3.3.3 Analytical Characteristics of the Proposed Method

#### 3.3.3.1 Linearity

With the described manifold and under the selected experimental conditions as shown in Table 3.12, a series of standard europium(III) solutions containing 0 to 10.0 ppm Eu(III) were studied. The results were shown in Table 3.13 and Figure 3.14. The calibration graph was linear in the concentration range up to 0.2 ppm and 2.0 - 3.0 ppm; above this range there was a slight but regular deviation from Beer's law.

**Table 3.12 :** Analytical characteristics for europium(III) determination with CTC.

| Analytical Characteristics | Information |
|---|---|
| conditions of the FI system | |
| conc. of CTC (M) | $4.0 \times 10^{-5}$ |
| conc. of Eu(III) (ppm) | 0 - 10 |
| injection volume (μl) | 100 |
| pH | 8.0 |
| flow rate of Eu(III) solution (ml/min) | 3.0 |
| flow rate of tris - buffer pH 8.0 (ml/min) | 3.0 |
| inner diameter of mixing tubing (in) | 0.0449 |
| length of mixing tubing (m) | 0.75 |
| shape of mixing part | s.b.s.r |
| conditions of detector | |
| absorbance range | 0 - 2 |
| conditions of recorder | |
| chart speed (min/cm) | 5 |
| sensitivity (mV/cm) | 20 |

**Table 3.13 :** Relationship between peak height and various concentrations of europium(III).

| Europium(III) concentration (ppm) | Peak height (mV)* | Europium(III) concentration (ppm) | Peak height (mV)* |
|---|---|---|---|
| 0.20 | 4.60 | 2.50 | 25.60 |
| 0.40 | 10.00 | 3.00 | 29.00 |
| 0.60 | 14.60 | 4.00 | 33.00 |
| 0.80 | 14.60 | 5.00 | 36.60 |
| 1.00 | 18.40 | 7.50 | 40.60 |
| 2.00 | 22.40 | 10.00 | 43.40 |

* average of triplicate results.

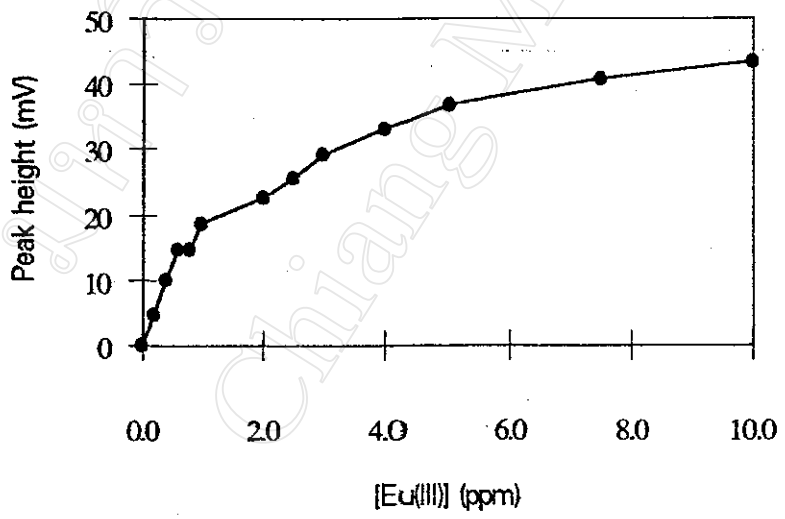


**Figure 3.14 :** The calibration curve for Eu(III) determination.

### 3.3.3.2 Precision

#### (i) Precision of instrument

This was investigated by repeating injection of standard europium(III) solution (100 µl) into a flowing merged stream of CTC and buffer solutions for 12 replicates. The results were summarized in Table 3.14. The relative standard deviation was 0.79%

**Table 3.14 :** Replicate determination of europium(III) solution (1.0 ppm).

| Experimental no. | Peak height (mV)* |
|---|---|
| 1 | 29.00 |
| 2 | 28.00 |
| 3 | 28.00 |
| 4 | 27.00 |
| 5 | 30.00 |
| 6 | 28.00 |
| 7 | 27.00 |
| 8 | 27.60 |
| 9 | 28.00 |
| 10 | 25.60 |
| 11 | 26.00 |
| 12 | 28.00 |
| $\bar{X}$ | 27.68 |
| S.D. | 1.20 |
| %R.S.D. | 4.32 |

* average of triplicate results.

### (ii) Precision of proposed method

The precision of the constructed FIA system obtainable for 12 determinations of 100 µl of the standard europium(III) solution containing 1.0 ppm of europium(III) was found to be 4.88% as shown in Table 3.15.

**Table 3.15 :** Replicate determination of 1.0 ppm of europium(III).

| Experimental no. | Peak height (mV)* |
|---|---|
| 1 | 27.40 |
| 2 | 28.40 |
| 3 | 26.60 |
| 4 | 26.00 |
| 5 | 27.60 |
| 6 | 27.00 |
| 7 | 24.40 |
| 8 | 25.40 |
| 9 | 25.00 |
| 10 | 24.60 |
| 11 | 25.00 |
| 12 | 25.00 |
| $\bar{X}$ | 26.03 |
| S.D. | 1.27 |
| %R.S.D. | 4.88 |

* average of triplicate results.

### 3.3.3.3 Detection limit

To estimate the detection limit, replicate injections of blank solution into the flowing merged streams of CTC and buffer solution. The data as shown in Table 3.16 indicated that the detection limit was equal to 0.010 ppm. This detection limit (0.010 ppm) could be confirmed by injecting 100 µl of standard solution containing varying low concentrations of europium(III) into the flowing merged streams of CTC and buffer solution. The results were presented in Table 3.17.

**Table 3.16 :** Peak height obtained for 12 replicates blank solution.

| Experimental no. | Peak height (mV)* |
|---|---|
| 1 | 145.00 |
| 2 | 143.00 |
| 3 | 144.00 |
| 4 | 144.40 |
| 5 | 145.00 |
| 6 | 144.00 |
| 7 | 144.00 |
| 8 | 145.00 |
| 9 | 145.00 |
| 10 | 143.00 |
| 11 | 143.00 |
| 12 | 142.00 |
| $\bar{X}$ | 143.95 |
| S.D. | 0.96 |
| %R.S.D. | 0.67 |

* average of triplicate results.

**Table 3.17 :** Peak height obtained for low concentration europium(III) solution.

| Europium(III) (ppm) | Peak height (mV)* |
|---|---|
| 0.003 | 144.00 |
| 0.005 | 145.00 |
| 0.010 | 147.40 |
| 0.020 | 147.80 |
| 0.030 | 148.00 |

* average of triplicate results.

### 3.3.3.4 Calibration curve and sensitivity

A linear calibration curve covering the concentration range 0.0 - 0.6 ppm of europium(III) under the recommended optimum conditions was established by plotting the peak height (Table 3.18 and Figure 3.15) against various concentrations of europium(III) as shown in Figure 3.15.

**Table 3.18 :** Peak height of various concentrations of Eu(III).

| Europium(III) (ppm) | Peak height (mV)* |
|---|---|
| 0.10 | 3.40 |
| 0.20 | 7.00 |
| 0.30 | 10.60 |
| 0.40 | 14.00 |
| 0.50 | 17.60 |
| 0.60 | 21.40 |

* average of triplicate results.

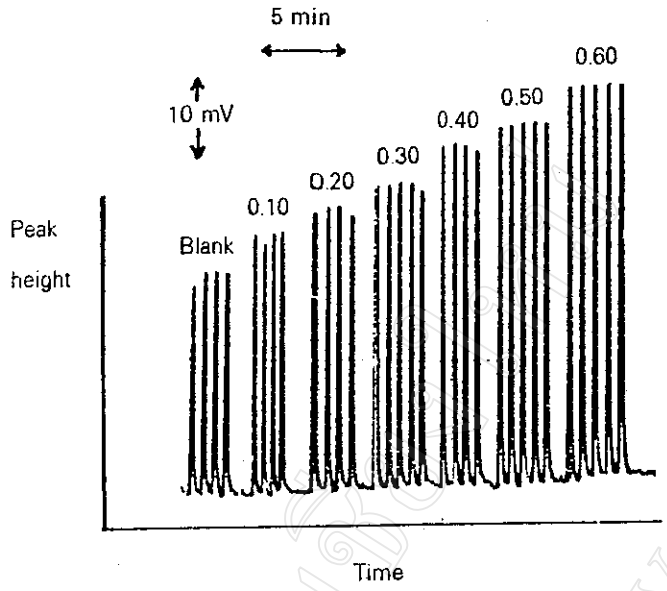


**Figure 3.15 :** FIA signals for 0 - 0.60 ppm of europium(III).

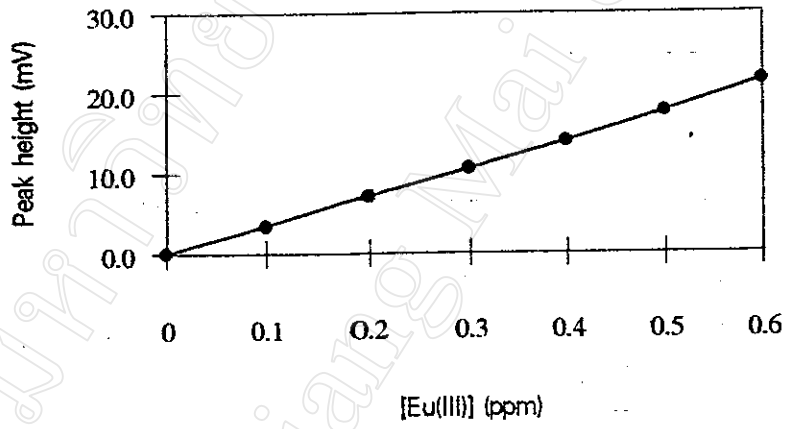


**Figure 3.16 :** The calibration curve for europium(III) determination with CTC.

From Table 3.18 and Figure 3.16, the calibration equation was calculated to be Y = 34.93X + 0.01. The slope and intercept were obtained with a correlation coefficient of 0.9994.

### 3.3.3.5 Accuracy

The accuracy of the proposed method was examined by standard addition method. The standard solutions containing four different concentrations of europium(III) were prepared and triplicate results were made on each standard europium(III) solution. The results were shown in Table 3.19. A mean recovery of 92.07% was found (range 88.0 - 96.0%)

**Table 3.19 :** Peak height obtained by using standard addition method.

| Europium | Net peak height (mV) | | Europium conc. (ppm) | | %Recovery |
|---|---|---|---|---|---|
| (ppm) | Std. Eu(III) | Std.+ sample | Graph | Found | |
| 0.00 | - | 4.60 | 0.132 | - | - |
| 0.10 | 3.40 | 8.00 | 0.228 | 0.096 | 96.00 |
| 0.30 | 10.60 | 14.00 | 0.396 | 0.264 | 88.00 |
| 0.50 | 17.60 | 21.00 | 0.593 | 0.461 | 92.20 |
| $\overline{X}$ | | | 92.07 | | |
| S.D. | | | 4.00 | | |
| %R.S.D. | | | 4.34 | | |

### 3.3.3.6 Interferences

In order to assess the possible analytical applications of the proposed method; the effect of some common interferences was studied by analysing standard solution containing 1.0 ppm of europium(III) and various amounts of each interference species. The results were tabulated in Table 3.20.

Table 3.20 : Relationship between peak heights and amounts of interfering species.

| Ion | Eu(III) : Ions | Peak height (mV) | %Relative error |
|---|---|---|---|
| Zn(II) | 1 : 0 | 15.60 | - |
| | 1 : 2 | 15.60 | 0 |
| | 1 : 5 | 15.60 | 0 |
| | 1 : 10 | 15.20 | -2.56 |
| | 1 : 20 | 15.00 | -3.85 |
| | 1 : 50 | 13.40 | -14.10 |
| Mg(II) | 1 : 0 | 15.60 | - |
| | 1 : 2 | 15.60 | 0 |
| | 1 : 5 | 16.00 | +2.56 |
| | 1 : 10 | 16.40 | +5.13 |
| | 1 : 20 | 17.00 | +8.97 |
| | 1 : 50 | 18.10 | +16.02 |
| | 1 : 100 | 19.00 | +21.79 |
| K | 1 : 0 | 15.60 | - |
| | 1 : 2 | 15.60 | 0 |
| | 1 : 5 | 15.60 | 0 |
| | 1 : 10 | 15.20 | -2.56 |
| | 1 : 20 | 15.00 | -3.85 |
| | 1 : 50 | 14.80 | -5.13 |
| | 1 : 100 | 14.00 | -10.26 |
| Al(III) | 1 : 0 | 16.00 | - |
| | 1 : 2 | 16.00 | 0 |
| | 1 : 5 | 15.60 | -2.50 |
| | 1 : 10 | 15.60 | -2.50 |
| | 1 : 20 | 15.00 | -6.25 |
| | 1 : 50 | 15.00 | -6.25 |
| | 1 : 100 | 14.00 | -12.50 |

Table 3.20 : (continued)

| Ion | Eu(III) : Ions | Peak height (mV) | %Relative error |
|---|---|---|---|
| Na | 1 : 0 | 16.00 | - |
| | 1 : 2 | 16.20 | +1.25 |
| | 1 : 5 | 16.50 | +3.12 |
| | 1 : 10 | 16.60 | +3.75 |
| | 1 : 20 | 17.00 | +6.25 |
| | 1 : 50 | 18.20 | +13.75 |
| | 1 : 100 | 18.20 | +13.75 |
| $SO_4^{2-}$ | 1 : 0 | 16.00 | - |
| | 1 : 2 | 16.00 | 0 |
| | 1 : 5 | 16.00 | 0 |
| | 1 : 10 | 16.00 | 0 |
| | 1 : 20 | 15.80 | -1.25 |
| | 1 : 50 | 15.80 | -1.25 |
| | 1 : 100 | 15.90 | -0.62 |
| $NO_3^-$ | 1 : 0 | 16.00 | - |
| | 1 : 2 | 16.00 | 0 |
| | 1 : 5 | 16.00 | 0 |
| | 1 : 10 | 15.90 | -0.62 |
| | 1 : 20 | 15.60 | -2.50 |
| | 1 : 50 | 15.60 | -2.50 |
| | 1 : 100 | 15.30 | -4.38 |
| $Cl^-$ | 1 : 0 | 16.00 | - |
| | 1 : 2 | 16.00 | 0 |
| | 1 : 5 | 16.20 | +1.25 |
| | 1 : 10 | 16.50 | +3.12 |
| | 1 : 20 | 16.45 | +2.81 |
| | 1 : 50 | 16.50 | +3.12 |
| | 1 : 100 | 17.00 | +6.25 |

## 3.4 Determination of europium(III) in spiked water samples

Spiked water samples containing various concentrations, viz., 0.005, 0.010, 0.050, 0.100, 0.300, 0.500, 0.700, 1.000, 2.000, 3.000 ppm europium(III), were analysed five times using the proposed method under the recommended conditions as shown in Table 3.12. The results are presented in Table 3.21.

**Table 3.21 :** Determination of europium(III) at different concentrations in spiked water samples using the proposed procedure.

| Sample no. | Concentration of europium(III) (ppm) | | %Recovery |
|---|---|---|---|
| | Added (ppm) | Found (ppm)* | |
| 1 | 0.005 | 0.005 | 100 |
| 2 | 0.010 | 0.011 | 110 |
| 3 | 0.050 | 0.053 | 106 |
| 4 | 0.100 | 0.109 | 109 |
| 5 | 0.300 | 0.302 | 101 |
| 6 | 0.500 | 0.495 | 99.0 |
| 7 | 0.700 | 0.675 | 96.4 |
| 8 | 1.000 | 0.980 | 98.0 |
| 9 | 2.000 | 1.778 | 88.9 |
| 10 | 3.000 | 2.700 | 90.0 |

* average of five determinations.

The results obtained with high percentage recoveries suggest that the proposed method is suitable for the determination of europium(III) in the samples.