

Studies on the Spectrophotometric Determination and Electrochemical Behavior of Heavy Lanthanide Ions in Nonaqueous System and Heavy Metal Chelate Complexes with Bidentate Legands: (Part I) Flow Injection Spectrophotometric Determination of Heavy Lanthanide Ions with Xylenol Orange

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Spectrophotometric determination of some heavy lanthanide ions by flow injection method is described. Xylenol Orange forms water soluble chelates with lanthanide ions in a tris[hydroxymethyl]-aminomethane-buffered medium having pH 8.3 and containing cetyltrimethylammonium bromide. The molar absorptivities of Ln(III)-XO complexes were increased by the ternary system with cetyltrimethylammonium bromide with the concomitant bathochromic shift of absorption maximum compared to those of the binary system without cetyltrimethylammonium bromide. The calibration curves are linear in the range 0.25-1.00 ppm for Gd(III), Dy(III), Er(III), Tm(III) and Yb(III) and the dynamic range are very wide. The detection limits ($S/N=2$) are from 2 ppb for Gd(III) to 30 ppb for Yb(III) and the relative standard deviations are from 1.2% for 0.5 ppm Gd(III) to 1.8% for 0.5 ppm Yb(III). The sample throughput was *ca.* 50 h^{-1} .

Introduction

Ternary systems containing of metal ion-metallochromic indicator-surfactant have found wide-spread use in spectrophotometric determination of trace concentrations of certain elements.¹⁻⁶ The popularity of such systems is due to both high sensitivity and colour contrast. Molar absorptivities can be dramatically increased by the presence of cationic or non-ionic surfactants, with the concomitant bathochromic shift of absorption maxima, compared to those of the binary systems without surfactants.

One of the early systems used for spectrophotometric determination of transition and lanthanide elements consisted of triphenylmethane dyes (xylenol orange, methylthymol blue, glycinecresol red and others) in the presence of cetylpyridium bromide and cetyltrimethylammonium bromide.⁷⁻¹² In addition, reagents such as chromeazurol S,^{13,14} eriochromeazurol B,¹⁵ bromopyrogallol red¹⁶ and eriochromecyanide R have been used.

In spite of the large number of papers that have been published on the practical use of ternary systems for the spectrophotometric determination of trace concentration of metal ions, there are few papers that have applied these ternary systems to flow injection analysis.

In our work, we have spectrophotometrically determined the concentration of some heavy lanthanide ions with xylenol orange in the presence of cationic surfactant, cetyltrimethylammonium bromide using flow injection method. The flow injection method is sensitive, reproducible and rapid compared to conventional procedure for spectrophotometric measurement.

Experimental

Reagents. All chemicals used were of analytical-reagent grade. All the reagent solutions were prepared with demineralized and double distilled water. Stock solutions (5.0

$\times 10^{-3}$ M) of Gd(III), Dy(III), Tm(III), Er(III) and Yb(III) were prepared by dissolving oxide form (Merk, 99.9%) in concentrated nitric acid and evaporated to dryness. The residue was dissolved in water to 100 ml. Stock xylenol orange solution (1.0×10^{-2} M) was prepared by dissolving 0.7606 g of xylenol orange (XO, BHD) in water and diluting to 100 ml. Stock cetyltrimethylammonium bromide solution (5.0×10^{-2} M) was prepared by dissolving of 9.1113 g of cetyltrimethylammonium bromide (CTAB, Sigma) in water and diluting to 500 ml. Buffer solutions were made from tris[hydroxymethyl]-aminomethane (Sigma) and the pH was adjusted with 1 M sodium hydroxide or hydrochloric acid. Carrier solution was 0.01 M hydrochloric acid.

Apparatus. For the batch method, the absorbance was measured with a Pye Unicam SP-400 UV/VIS spectrophotometer. A Corning pH meter 200 was used to measure pH. For the flow injection manifold, a Sanuki Kogyo Model DMX-2000 double-plunger micro-pump was employed with a Soma visible spectrophotometric detector, Model 5-3250 (8 μ l flow cell) and a Philips, PM 8261 chart recorder.

Flow Injection Procedure. The manifold of the flow injection system here is shown in Figure 1. The reagent (XO + CTAB + Buffer) and the carrier solution (0.01 M HCl) were pumped at 1.16 $ml\ min^{-1}$. The sample (100 μ l) containing lanthanide ions was injected into the carrier stream by six-way injection valve and mixed with the reagents in the reaction coil. After the colour was developed in the reaction coil, the absorbance was monitored at 610 nm by a spectrophotometric detector fitted with a micro flow cell (8 μ l, 10 mm path length) and recorded peak-shaped signals.

Results and Discussion

Absorption Spectra. Ln(III) forms a violet colored complex with XO in alkaline solution. As can be seen in the Figure 2, Ln(III)-complexes with XO in the absence of CTAB have absorption maximum at *ca.* 570 nm in pH 8.3 using

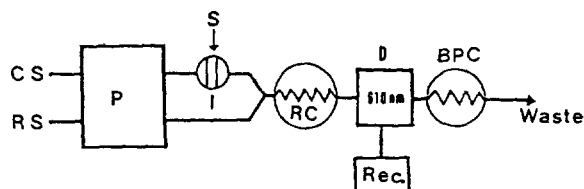


Figure 1. Schematic diagram of the flow-injection manifold. CS: Carrier solution, RS: Reagent solution, P: Double plunger micro-pump, I: Six-way valve sample injector (sample volume: 100 μ l), S: Sample, RC: Reaction coil (i.d. 0.2 mm, length 50 cm), D: Spectrophotometric detector (flow cell: 8 μ l, 10 mm), Rec: Recorder, BPC: Back-pressure coil (i.d. 0.2 mm, length 100 cm).

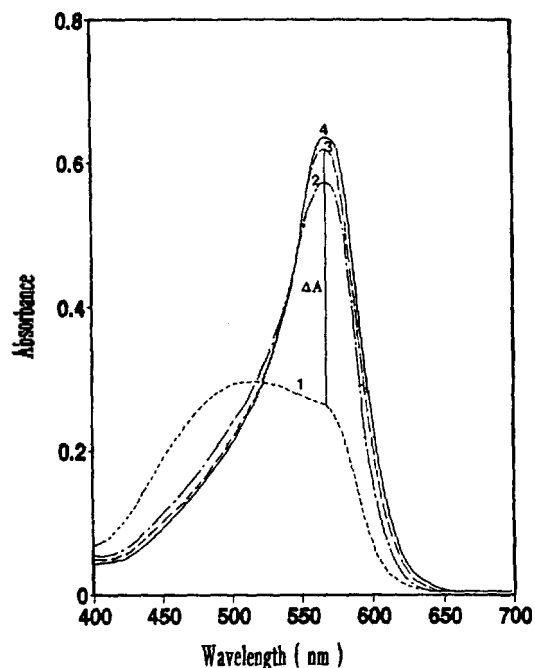


Figure 2. Absorption spectra of Ln(III)-XO complexes. Curves, 1: Reagent (XO), 2: Gd(III)+XO, 3: Er(III)+XO, 4: Yb(III)+XO, Concentration, XO: 2.0×10^{-5} M, Ln(III): 6.0×10^{-6} M, pH: 8.3 (0.3 M Tris buffer), Blank: Water

water blank as reference. At this wavelength, the absorption of XO is also observed very strongly. Figure 3 shows the absorption spectra of Ln(III)-XO complexes in the presence of CTAB at pH 8.3. The maximum absorbances appear at ca. 600 nm and the molar absorptivities are increased in the ternary system with CTAB compared to those of the binary system without CTAB. The differences (ΔA) of absorbances between the complexes and reagents at the maximum wavelength are larger in the presence of CTAB than those in the absence of CTAB. So, the detection response in FIA system is more sensitive in the ternary system with CTAB than that in the binary system without CTAB as shown in Figure 2 and 3. In this work, the wavelength of spectrophotometric detection in FIA system was chosen at 610 nm because the differences (ΔA) were the largest in this region. From the investigation of pH effect on the formation of Ln(III)-XO complexes in CTAB, the absorbances were obta-

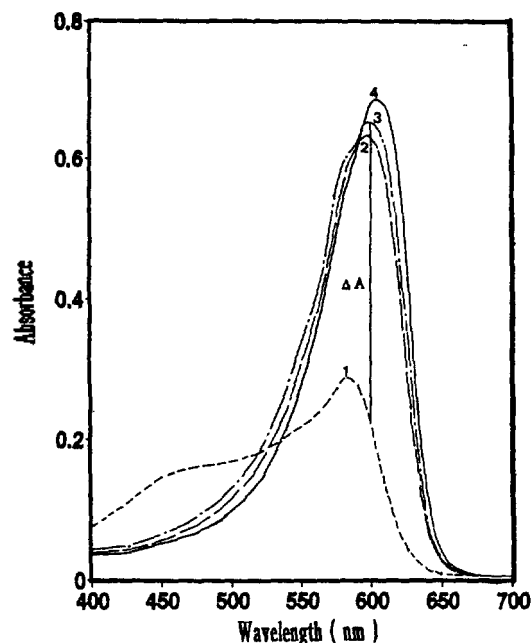


Figure 3. Absorption spectra of Ln(III)-XO in presence of CTAB. Curve, 1: Reagent (XO+CTAB), 2: Yb(III)+XO+CTAB, 3: Er(III)+XO+CTAB, 4: Gd(III)+XO+CTAB, Concentration, Ln(III): 6.0×10^{-6} M, XO: 2.0×10^{-5} M, CTAB: 1.5×10^{-3} M, pH: 8.3 (0.3 M Tris buffer), Blank: Water.

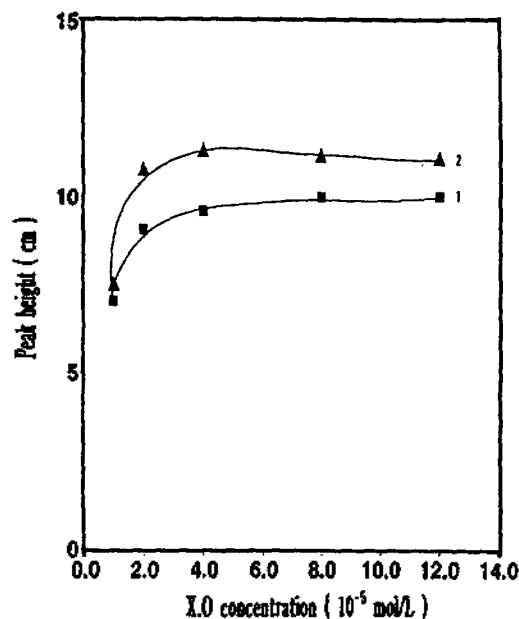


Figure 4. Effect of XO concentration on the intensity of peak heights. Sample, 1: Gd(III), 2: Er(III). Concentration: 6.0×10^{-6} M, Reagent solution: XO+ 2.0×10^{-5} M CTAB, pH: 8.3 (0.3 M Tris buffer), Flow rate: 1.0 ml min $^{-1}$.

ined to be maxima and constant in the range of pH 8.0-8.5 (0.3 M Tris buffer).

Effect of XO Concentration in FIA System. The effect of XO concentration on the peak height examined by varying the concentration of XO from 1×10^{-5} M to 1.2×10^{-4}

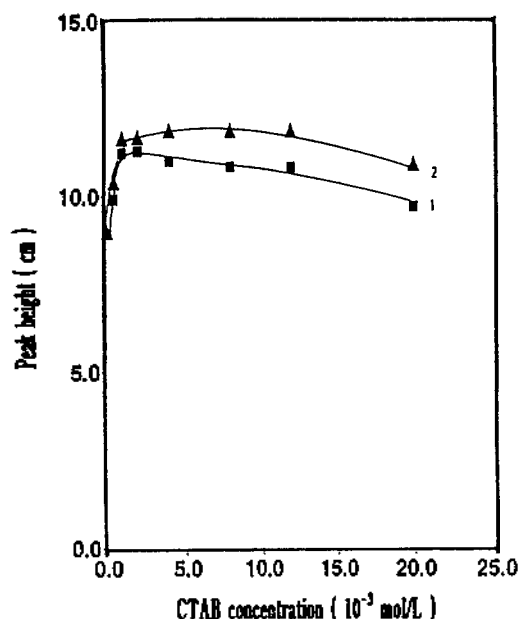


Figure 5. Effect of CTAB concentration on the intensity of peak heights. Sample, 1: Gd(III), 2: Er(III), Concentration: 6.0×10^{-6} M, Reagent solution: 4×10^{-5} M XO+CTAB, pH: 8.3 (0.3 M Tris buffer), Flow rate: 1.0 ml min^{-1} .

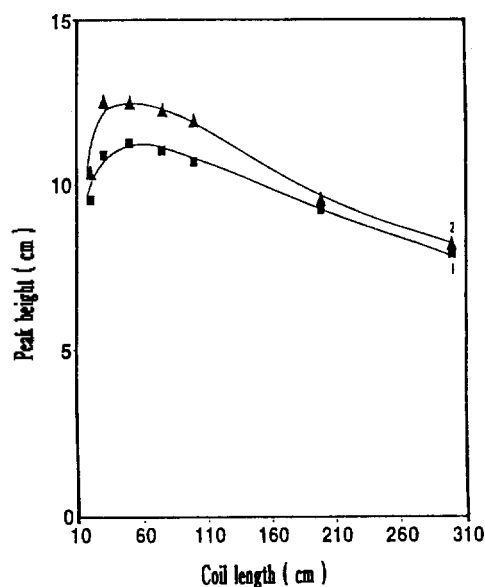


Figure 6. Effect of the reaction coil lengths on the intensity of peak heights. Sample, 1: Gd(III), 2: Er(III), Concentration: 6.0×10^{-6} M, Reagent solution: 4×10^{-5} M XO+ 2.0×10^{-3} M CTAB, pH: 8.3 (0.3 M Tris buffer), Flow rate: 1.0 ml min^{-1} .

M using 1.0×10^{-2} M HCl as carrier at 1.0 ml min^{-1} . The peak heights were almost constant and the largest at concentration above 4.0×10^{-5} M as shown in Figure 4. However, when XO concentration was increased more than 4.0×10^{-4} M, the background signal became larger and unstable. In this work, 4.0×10^{-5} M XO was chosen for the further use.

Effect of CTAB Concentration. The effect of CTAB concentration on the peak height in FIA was investigated

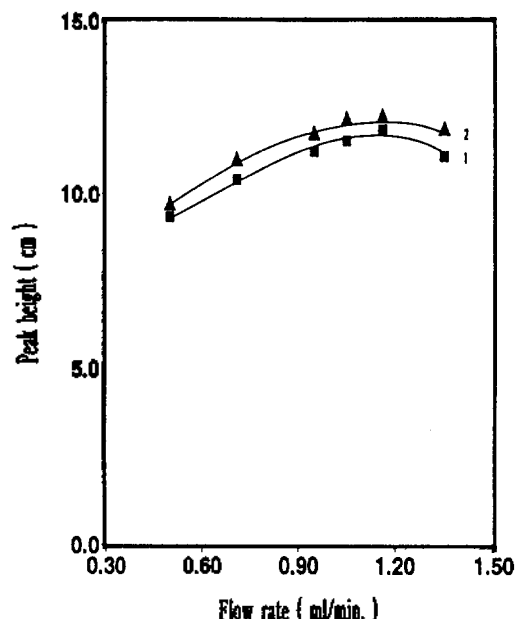


Figure 7. Effect of flow-rate on the intensity of peak heights. Sample, 1: Gd(III), 2: Er(III), Concentration: 6.0×10^{-6} M, Reagent solution: 4×10^{-5} M XO+ 2.0×10^{-3} M CTAB, pH: 8.3 (0.3 M Tris buffer).

in the range of 1.0×10^{-4} M to 2.0×10^{-2} M. As can be seen Figure 5, the largest and the most constant peak height was observed in the region of 1.0×10^{-3} M to 2.0×10^{-3} M concentration. This concentration is near to CMC (ca. 1.0×10^{-3} M) of CTAB. Above 2.0×10^{-3} M CTAB, the peak heights are generally decreased with increase of CTAB concentration. Therefore, 2.0×10^{-3} M CTAB was used as the optimum experimental concentration.

Effect of Reaction Coil Lengths. Figure 6 shows response curves of peak height obtained by injecting the sample of lanthanide ions at different length of reaction coils. The reaction coil length was varied in the range of 20-300 cm. It can be seen that the coil length has a considerable effect on the peak heights. The peak height of samples was increased with increasing reaction coil length in the range of 20 cm to 50 cm because the larger residential time of the sample zone allowed greater complex formation. However, the peak height lowering and broadening were observed at longer coil length from 60 cm to 300 cm. This effect is due to the excessive dispersion of the sample zone in the long reaction coil. A 50 cm coil length was the best choice because the maximum peak height showed in this length.

Effect of Flow Rate of Reagent Solution. The effect of flow rate on peak heights is shown in Figure 7. The flow rate had a considerable influence on the peak height. The peak height lowering was observed both low and high flow rate with maximum peak height at flow rate of 1.16 ml min^{-1} . At low flow rate below maximum peak height, the sample zone disperses greatly in the reaction coil with decreasing the flow rate and therefore, excessive dispersion of the sample zone caused broadening, tailing and lowering of the absorption signal. At high flow rate above maximum peak height, the sample zone flows out from the reaction coil fastly and the residential time of sample zone in the

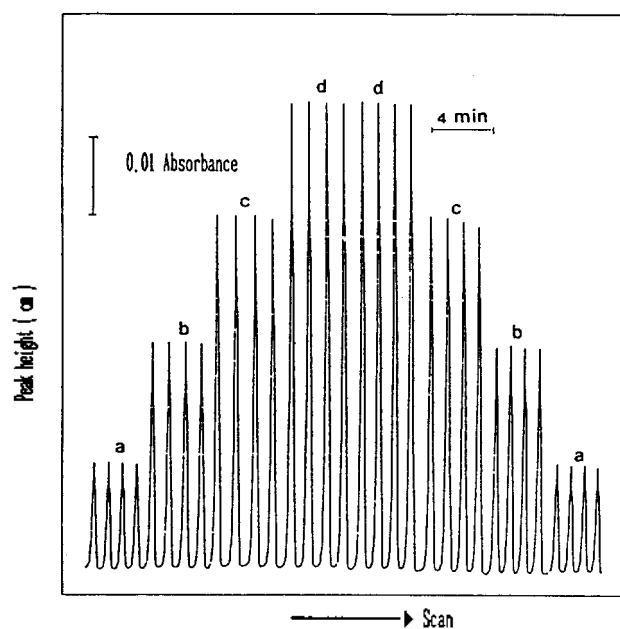


Figure 8. Flow signals for calibration graph of Dy(III) under optimum condition. Reagent solution: 4×10^{-5} M XO + 2.0×10^{-3} M CTAB, pH: 8.3 (0.3 M Tris buffer), Carrier solution: 0.01 M HCl, Flow rate: 1.16 ml/min, Reaction coil length: 50 cm. a: 0.25 ppm, b: 0.50 ppm, c: 0.075 ppm, d: 1.00 ppm.

Table 1. Calibration Curves for Some Ln(III) Ions

Metal	Linear regression parameters				Detection limits ppb (S/N=2)
	Slope	Intercept	Correl. coef.	Range of conc. ppm	
Gd(III)	18.49	-1.075	0.9994	0.25-1.00	2 ppb
Dy(III)	15.37	-0.4338	0.9998	0.25-1.00	3 ppb
Er(III)	19.81	-1.113	0.9988	0.25-1.00	2 ppb
Tm(III)	11.55	-0.2625	0.9987	0.25-1.00	4 ppb
Yb(III)	7.40	-0.2500	0.9983	0.25-1.00	30 ppb

Experimental conditions are the same as in Figure 8. The values are the mean of eight trials.

reaction coil reduces with increasing the flow rate. Therefore, the peak height was also decreased since Ln(III)-XO complexes could not form perfectly in the reaction coil.

Calibration Curve. Under optimum condition recommended by above investigation for flow injection parameters, the typical calibration curve was obtained. Figure 8 shows the recorder traces for a series of runs of Dy(III). The calibration curve was linear in the range of 0.25-1.0 ppm and the dynamic range was very wide (0.01-20.0 ppm). The detection limit (S/N=2) was 3 ppb. The relative standard deviation

was 1.2% for eight trials of 0.5 ppm Dy(III). The linear regression parameters for calibration curves of some Ln(III) ions are summarized in Table 1. As can be seen from the data in Table 1, the regression parameters for calibration curves exhibit linearity, sensitivity and detection limit in the given concentration range. The correlation coefficients are about 0.9998-0.9983. The detection limits were from 2 ppb for Gd(III) to 30 ppb for Yb(III).

Interferences. Most of lanthanide ions which form coloured complexes with XO in the presence of CTAB interfered in their coexistent state each other owing to spectral overlap as shown in Figure 3. A preliminary separation of lanthanides ions would be necessary for the determination of them. Some transition metals such as copper, nickel, iron and cadmium ions also interfered seriously more than 1.0 ppm. The elimination of such interferences was attempted using several masking agents, but it was not quite fruitful so far. Therefore, the determination of lanthanide ions with this FIA method would be performed after the separation of them by ion exchange chromatography when they coexist.

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