

Spectrophotometric Determination of Scandium(III) in Monazite after Separation Using Amberlite IRC 718 Chelating Resin

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Received June 11, 1999

The spectrophotometric determination method of scandium with eriochrome cyanine R (ECR) and the composition ratio of the complex were investigated in the presence of surfactants. A volume of 5 mL of 1.0×10^{-3} M ECR and 10 mL of 2.0×10^{-1} M CTMAB are necessary for the determination of $1.0 \times 10^{-7} \sim 3.0 \times 10^{-6}$ M Sc(III) at pH 6.5. The apparent molar absorption coefficient of the Sc(III)-ECR-CTMAB, ternary complex at 610 nm is $5.6 \times 10^5 \text{ mol}^{-1} \text{ cm}^{-1} \text{ L}$ and its detection limit is 1.0×10^{-7} M. Separation studies were conducted by the column method. The effect of pH, elution solution and the influence of rare earth elements as interferences was discussed. Their separation was carried out in 0.1 M HCl-50% methanol solution and 1.0 M HCl media. The method was applied for the determination of Sc(III) in monazite.

Introduction

Triphenylmethane dye has been extensively used for the spectrophotometric determination of scandium ion. Numerous methods such as arsenazo III,¹ chrome azurol S (CAS),² methyl thymol blue (MTB),³ xylenol orange (XO)⁴⁻⁶ are available for the spectrophotometric determination of scandium ion. Typically, those metal-dye complexes have molar absorptivities ranged $1.0\text{-}5.0 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1} \text{ L}$.

The sensitivity of spectrophotometric determination is often enhanced by addition of surfactants to metal-dye complex solution. The sensitization effect is characterized by an increase in molar absorptivity and red shifts of λ_{max} (approximately 50-150 nm).^{7,8} Generally, there are two models for sensitization mechanism: micellar solubilization and formation of ternary complexes containing surfactant monomers. Micelles have been widely applied to many areas of science and technology.⁹⁻¹² One of the well known abilities of them is to make water-insoluble compounds to soluble. Because hydrophobic molecules are surrounded by the micelles, it can be soluble in aqueous media.¹³

ECR [I], sodium 2''-sulpho-3,3'-dimethyl-4-hydroxyfuchson-5,5'-dicarboxylate, a dye in the triphenylmethane series has been used for spectrophotometric determination of Aluminium(III), Beryllium(II) and others. It has been reported that addition of 2,2'-bipyridine (bpy) to ECR enhance the sensitivity and selectivity for iron(II).¹⁴

In this paper, we focused on careful examination of the spectrophotometric behaviors of Sc(III)-ECR complex in the various surfactants (cationic, anionic and nonionic). The other intention of this study was to improve the understanding those mechanisms underlying surfactant sensitization. And, this paper describes the spectrophotometric determination of Sc(III) by ECR with separation of Sc(III) using Amberlite IRC-718 resin. One of the few commercial chelating ion exchange resins available is Amberlite IRC-718 of which the chelating ability is attributed to iminodiacetic acid groups. Very little evaluation has been performed

on this exchanger. The present paper gives the adsorption capacities for Sc(III) and some other rare earth elements between Amberlite IRC-718 resin and inorganic acid solutions and applies the results to quantitative separation of metal ions. The present method is a highly sensitive and simple for separation and spectrophotometric determination of Sc(III).

Experimental Section

Apparatus. Absorption spectra were measured with recording spectrophotometer, Perkin-Elmer Model 552S, with 1 cm quartz cells. Jovin Yvon instruments SA 24 inductively-coupled plasma atomic emission spectrometry (ICP-AES) was used for metal determination. All pH measurements were made with a NOVA-310 pH meter. The resin used in the column was Amberlite IRC-718, 16-50 mesh. The resin was washed successively with 6 M HCl, water, 1 M NaOH, water, 1 M HCl and water in order to remove organic and inorganic contaminants.

Reagent. Analytical-reagent grade chemicals and distilled, deionized water were used throughout. Stock solution of Sc(III) (1.0×10^{-1} M) was prepared from Sc_2O_3 (Sigma, 99.9% purity). Weighed amount of Sc_2O_3 was dissolved with 0.1 M hydrochloric acid and diluted to a constant volume with water.

Stock solution of ECR (1.0×10^{-3} M) was prepared by dissolving 0.536 g of ECR in 1 L water. The cetyltrimethylammonium bromide (CTMAB, 99%: sigma) and sodium dodecyl sulfate (SDS, 99%: sigma) were used without additional purification. The Triton X-100 (octylphenoxy polyethoxyethanol) used in this study was obtained from Sigma Co. and used as received. An average molecular weight of 624 g mol^{-1} was used for concentration calculation.

The surfactant solutions were prepared as 1.0×10^{-3} M. The sample solution was adjusted to pH 6.5 with hexamethylenetetramine (HTM) buffer and the surfactants should not have any absorbance from 400 to 800 nm.

Procedure

Spectrophotometric determination. An aliquot of Sc(III) standard solution was transferred to a 50 mL volumetric flask, consecutively 5.0 mL of the 1.0×10^{-3} M ECR solution, 3.0 mL of pH 6.5 hexamethylenetetramine (HTM) buffer and 10 mL of 2.0×10^{-4} M surfactant solution were added. The solution was made up to the mark with distilled water. The absorbance of the solution was measured at 400-800 nm against a reagent blank as a reference.

Separation.

Column: A glass separation column (25×150 mm) having a stopcock was packed with 10 g of the resin. The resin was regenerated with 6.0 M HCl and a large volume of water.

Batch procedure: Resin (1.0 g) and 50 mL solution of La(III), Sm(III), U(IV), Nd(III) and Sc(III) in a 100 mL beaker were stirred moderately for 24 hr at room temperature. After equilibrium, the solution was filtered through Whatman #2 filter paper. The filtrate was diluted with water and the concentration of metal ions was determined by ICP-AES.

Column procedure: Separation of metal ions in the column system was carried out under the following conditions. A fixed volume of aqueous solution of the metal ions was adjusted to a suitable pH and percolated through the column at a flow rate of 1.0 ± 0.2 mL min^{-1} . La(III), Sm(III) and Nd(III) was eluted with 0.1 M HCl-50% methanol solution and Sc(III) with 1.0 M HCl. Sc(III) was determined spectrophotometrically.

Results and Discussion

The spectral characteristics, effect of variables and diverse ions on Sc(III)-ECR absorbance and applications of the system are discussed below.

Spectrophotometric determination. The absorption spectra of the ECR ligand were studied at various pH adjusted with buffer solutions. ECR have absorption maxima λ_{max} at 422 nm in pH 7-9, 476 nm in pH 1-4 and 580 nm in pH > 11.9 solution. The changes of λ_{max} from 420 nm to 580 nm according to pH could be interpreted in terms of increasing dissociation ratio of protons from ECR.

The absorption spectra of complexes between ECR and several metal ions at pH 6.5 were shown in Figure 1. As shown in Figure 1, λ_{max} of ECR-metal complexes were similar to ECR^+ species. The effect of pH on the absorbance of Sc(III)-ECR complex at 610 nm is shown in Figure 2. The results indicate that maximum absorbance was obtained at pH 6.2-6.8. In more acidic or more alkaline solutions, absorbances decreased because of incomplete complex formation and of hydrolysis of the complex.

The effects of cationic surfactants [cetyltrimethylammonium bromide (CTMAB), dodecyltrimethylammonium bromide (DTMAB)], nonionic surfactants [Brij 58, Triton X-100] and anionic surfactant [sodium dodecyl sulfate (SDS)] were studied. The results indicated that the remarkable

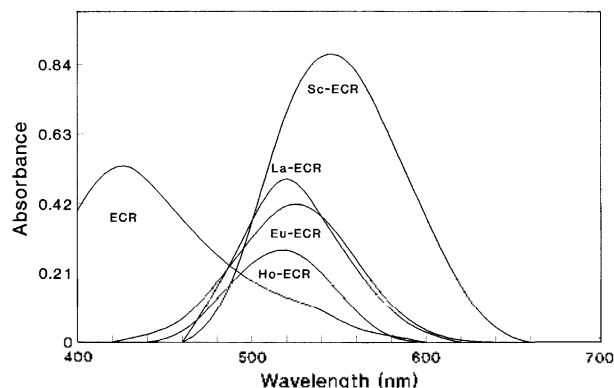


Figure 1. Absorption spectra of ECR and ECR-Metal complex at pH 6.5. Metal: $5 \mu\text{g/mL}$, ECR: 1.0×10^{-4} M.

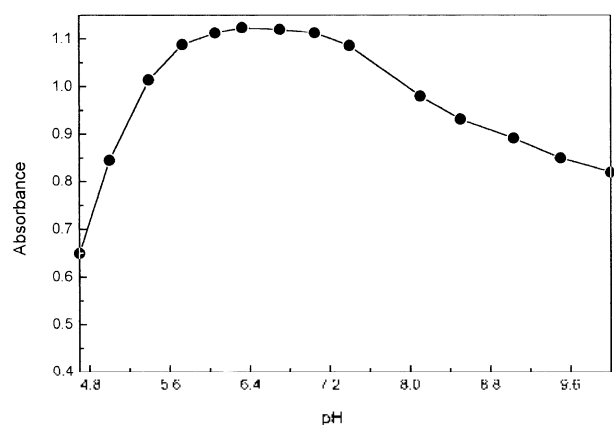


Figure 2. Effect of pH, Sc(III): 2.0×10^{-6} M, ECR: 1.0×10^{-4} M, CTMAB: 2.0×10^{-4} M.

absorbance increase of Sc(III)-ECR system were made in the CTMAB surfactant but same effects were not found in anionic surfactant and nonionic surfactant. The use of the surfactant combination of CTMAB as cationic surfactant was most effective and the color development was stable and reproducible. The addition of CTMAB to the Sc(III)-ECR solution led to the red-shift of λ_{max} (608-615 nm) and an increase of absorbance at λ_{max} . The absorbance of Sc(III)-ECR complex increased with an increase of CTMAB concentration up to 1.2×10^{-4} M. The approximately constant absorbance was obtained in higher concentration than 1.2×10^{-4} M. Thus, 2.0×10^{-4} M CTMAB was chosen as an optimum experimental condition. The enhancement factor (absorbance of Sc(III)-ECR-CTMAB vs that of Sc(III)-ECR) was calculated as 7 times in the 2.0×10^{-4} M CTMAB solution. The mechanism of the red shift and absorbance increase in the presence of CTMAB can be interpreted with the formation of Sc(III)-ECR-CTMAB ternary complex.

In order to study the composition of Sc(III)-ECR-CTMAB ternary complex, we measured the mole ratio of Sc(III) and ECR in Sc(III)-ECR complex with and without CTMAB. The molar composition of the Sc(III)-ECR complex was ascertained using the continuous variation method. The molar composition of the Sc(III) to ECR was 1 : 2 in the absence of CTMAB and 1 : 3 in the presence of CTMAB. The stoichio-

Table 1. Tolerance limit to diverse ions on the recovery of 1.0 mg Sc(III)

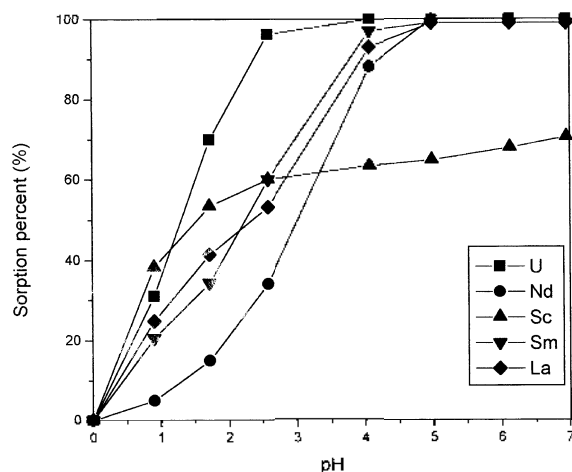
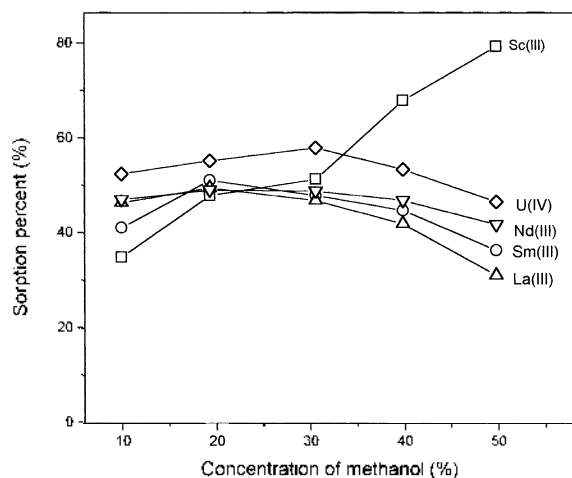
Tolerance limit (ppm)	Foreign ions
2.5	Ho(III), Y(III)
1	Nd(III), Eu(III), U(IV)
0.5	La(III), Sm(III)

metric mole ratio of Sc(III) and ECR of Sc(III)-ECR complex changed from 1 : 2 to 1 : 3 in the presence of CTMAB. The molar ratio of Sc(III) and CTMAB in the Sc(III)-ECR-CTMAB complex was determined by the method mentioned above. It appeared that the molar ratio of Sc(III) and CTMAB in the ternary complex of Sc(III)-ECR-CTMAB was 1 : 1. The positive charge of the cationic surfactant would attract the negatively charge complex or mixed-ligand complex, so 1 : 1 (mole ratio) complex of CTMAB and Sc(III)-ECR was formed.

The calibration curve for the determination of Sc(III) by this method was prepared in the range of 1.0×10^{-7} M to 3.0×10^{-6} M. The equation obtained by least-squares method ($n = 11$) is: $A = 5.61 \times 10^5 C + 0.003$ ($r = 0.9996$), where A is the absorbance, C is molarity of scandium and r is the correlation coefficient. The calculated molar absorptivity is $5.61 \times 10^5 \text{ mol}^{-1} \text{ cm}^{-1} \text{ L}$.

The selectivity in the proposed method was investigated by determining $1.0 \mu\text{g/mL}$ of Sc(III) in the presence of various rare earth elements. Interference was regarded as significant when it produced a difference of more than +3% in absorbance from that found with Sc(III) ion alone. The results are given in Table 1. The results indicated that the concentration range of $1.0\text{-}0.5 \mu\text{g/mL}$ for La(III), Sm(III), Eu(III) and U(IV) are upper limits for interference. Therefore, it can be understood that the separation of Sc(III) from the matrix is necessary prior to spectrophotometric determination. For this purpose, a column separation method was investigated.

Column separation method. The adsorption capacity to pH (Amberlite IRC-718 resin) profiles for U(IV), La(III), Sm(III), Nd(III) and Sc(III) are given in Figure 3. Figure 3 shows that adsorption depends apparently on the pH of the solution due to the competing protonation and complexation reactions of the functional group (iminodiacetic acid) of resin. Sc(III) ion adsorption capacity, as shown by adsorption percent at pH 5.0 (Figure 3), is 70%, but adsorption capacity of other ions are almost 100%. In Figure 4, the influence of alcohol concentration on the sorption capacity is shown by taking methanol as examples. Figure 4 shows that the linear increase of sorption capacity with increasing percentage of alcohol is interrupted in the case of Sc(III) at the alcohol concentration of 10% and 50%. The sorption capacities of Sc(III), U(IV), Nd(III), Sm(III) and La(III) studied slightly increase with increasing proportions of methanol at low percentages of methanol (10-30%). At higher percentages of methanol, however, the sorption capacities of U(IV), Nd(III), Sm(III) and La(III) ions were decreased but, Sc(III) having the smallest ionic radius showed the highest affinity

**Figure 3.** Effect of pH on the sorption of metal ions with Amberlite-718 resin. Resin weight: 500 mg. Conc. of each metal ion: $1.0 \text{ mg}/50 \text{ mL}$. Shaking time: 24 hrs.**Figure 4.** Effect of methanol concentration on the sorption of rare earth elements. Resin weight: 500 mg. Conc. of each metal ion: $1.0 \text{ mg}/50 \text{ mL}$. Matrix: 0.1 M HCl . Shaking time: 24 hrs.

to the Amberlite IRC 718 chelating resin. From Figure 4 it seems that Sc(III) can easily be separated from Sm(III), La(III), Ce(IV) and Nd(III), by using 50% methanol medium as the elution solution. The sorption capacities of the resin toward metal ions were found to depend on the HCl concentration of the sample solutions. For Sc(III) ion the capacity decreased gradually with increasing the HCl concentration from 0.1 to 1.0 M. The effect of flow rate of the sample loading through the column was studied over the range $0.5\text{-}2.0 \text{ mL min}^{-1}$. The adsorption of metal ions remains almost unchanged regardless of any change in the flow rate. In subsequent experiments a flow rate of $1.0 \pm 0.2 \text{ mL min}^{-1}$ was maintained for both adsorption and elution. From the results presented in Figure 4, HCl-methanol mixture and HCl solution have been considered as an eluent for the separation of the synthetic metal solution. The column was equilibrated with acetic acid buffer of pH 5.0. 8 mL sample solution containing 250 ppm of each metal ion was loaded onto the column (Figure 5) and La(III), Sm(III) and Nd(III) was eluted

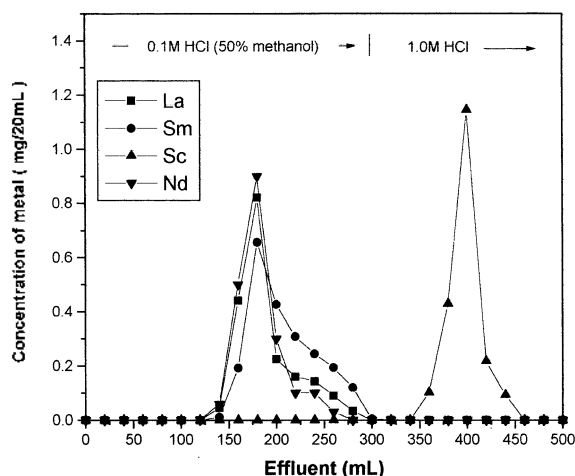


Figure 5. Elution curve of Sc(III), La(III), Sm(III) and U(IV). Resin: Amberlite IRC-718 chelating resin. Loading: 2.0 mg of Sc(III), La(III), Nd(III) and Sm(III) in 8 mL. Elution: 0.1 M HCl-50% methanol solution and 1.0 M HCl. Flow rate: 1.00.1 mL min⁻¹.

Table 2. The results of Sc(III) spiked monazite digest solution analysis

Sc(III) spiked (mg/100 mL)	Sc(III) Found (mg/100 mL)	Recovery (%)
0	—	—
10.0	9.4	94.0
20.0	18.7	93.5

matrix composition (mg/100 mL): Ce(IV): 310, La(III): 231, Pr(III): 4, Nd(III): 9, Sm(III): 0.3, Y(III): 8.

with 300 mL of 0.1 M HCl-50% methanol solution. Then 200 mL of 1.0 M HCl was used to elute Sc(III). The effluent of 200 mL of 1.0 M HCl was used directly for the spectrophotometric determination of Sc(III) as the complex at 610 nm and Sm(III), La(III) and Nd(III) concentration were determined by ICP-AES.

Results of monazite sample analysis. The present method has been applied to the analysis of a monazite sand sample. 2 g of the sample was completely dissolved in a minimum volume of concentrated sulfuric acid (about 20 mL) by heating on a water bath. The solution was evaporated to near dryness. To this a small volume of water was added. The solution was cooled, filtered and diluted to 100 mL (0.1 M HCl). The results of monazite sample analysis are shown in Table 2. In the Table, the results of Sc(III) spiked monazite digest solutions are also shown since Sc(III) concentration in the

monazite is below detection limit, 0.045 mg/100 mL. The found value is agree with the spiked value.

Conclusion

The spectrophotometric determination method of Sc(III) has been investigated after separation of Sc(III) from the mixed ions using Amberlite IRC-718 resin. The complex between ECR and Sc(III) in the presence of CTMAB is very stable and more sensitive than that in the absence of surfactant. The calibration line of Sc(III) is obtained over the range 1.0×10^{-7} – 3.0×10^{-6} M. The apparent molar absorption coefficient and the detection limit of Sc(III)-ECR-CTMAB at 610nm is 5.61×10^5 mol⁻¹cm⁻¹L, and 1.0×10^{-7} M, respectively. The enhancement factor of Sc(III)-ECR-CTMAB over Sc(III)-ECR is 7.0. The method was applied for the determination of Sc(III) in monazite.

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