Spectrophotometric Determination of Scandium(III) with *o*-Hydroxyhydroquinonephthalein in Cationic Micellar Media

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Synopsis. A spectrophotometric method for determining trace amounts of scandium(III) has been established which makes use of formation of its ternary complex with *o*-hydroxyhydroquinonephthalein (Qnph) and *N*-hexadecylpyridinium chloride (HPC) as a cationic surfactant at pH 5.4. The molar ratio of the ternary complex among Qnph, scandium(III), and HPC is 3:2:6 in a weakly acidic medium, and its maximum absorbance is at 555 nm against a reagent blank. Beer's law holds in the concentration range 0—4.5 μg of scandium(III) in a final volume of 10 cm^3 at 555 nm. The apparent molar absorptivity is 1.0×10^5 dm^3 mol^{-1} cm^{-1} with a Sandell sensitivity of 0.0005 μg cm^{-2}. The coefficient of variation was 0.6% (n=5) for 2.7 μg of scandium(III).

Ternary complex formation reactions among organic reagents, metal ions, and cationic surfactants have proved[1—4] to result in markedly improved spectrophotometric properties–high molar absorptivity, stability over a wide pH range, and large bathochromic shift–in comparison with binary complex formation reactions between organic reagents and metal ions.

For scandium(III), various spectrophotometric determinations using Xylenol Orange (XO),[5] Methylthymol Blue (MTB),[6] Arsenazo III,[7] or Bromopyrogallol Red (BPR)[8] have been reported. However, most of these methods have disadvantages such as lacks in reproducibility, selectivity, or simplicity.

We have already reported that *o*-hydroxyhydroquinonephthalein (Qnph) is a useful reagent for spectrophotometric determination of various metal ions.[9—13] We have also noticed that similar methods utilizing cationic surfactants such as *N*-hexadecylpyridinium chloride (HPC) and *N*-hexadecyltrimethylammonium chloride (HTAC) are in lower pH regions, very sensitive, sharp in selectivity, and excellent in repeatability, in comparison with methods utilizing binary complex formation reactions without cationic surfactants.

In the present research, color reactions between Qnph and scandium(III) in the presence of various surfactants were first studied, and then essential conditions for simple, rapid, and sensitive spectrophotometric determination of scandium(III) were established with Qnph in the presence of cationic surfactant.

Experimental

Absorption spectra and absorbances were measured with recording spectrophotometers, Shimadzu Model UV-200 and UV-240 and a Hitachi Model 150-20, with 1.0 cm silica cells. Hitachi-Horiba Model F-7AD and M-5 pH glass electrode meters were used for pH measurement.

A 1.0×10^{-3} mol dm^{-3} solution of Qnph was prepared according to Ref. 9 and stored in a brown bottle. A stock solution (1.0×10^{-2} mol dm^{-3}) of scandium(III) was prepared by dissolving scandium chloride with a small amount of hydrochloric acid and deionized water. The concentration of the stock solution was determined by chelatometric titration, and a working solution (5.0×10^{-4} mol dm^{-3}) was prepared by dilution of this stock solution. A 1.0×10^{-2} mol dm^{-3} HPC solution was prepared by dissolving HPC in 20% methanol or water. Sodium acetate-acetic acid buffer solution 2.0×10^{-1} mol dm^{-3}; pH 5.4 was used for pH adjustment.

All the other reagents and materials were of analytical grade and used without further purification. Deionized water was used.

To a series of solutions containing 0—4.5 μg of scandium(III) were added 2.0 cm^3 of 1.0×10^{-2} mol dm^{-3} HPC solution, 3.0 cm^3 of sodium acetate-acetic acid buffer solution (pH 5.4), and 1.5 cm^3 of 1.0×10^{-3} mol dm^{-3} Qnph solution, mixed and diluted in several 10 cm^3 calibrated flasks to obtain suitable working solutions. After 10 min, the absorbance of the Qnph–scandium(III) complex solution was measured at 555 nm against a reagent blank (Qnph solution). The concentration of scandium(III) was determined by using a calibration graph.

Results and Discussion

In Fig. 1, curves A, B, C, and D show absorption spectra of Qnph and Qnph–scandium(III) complex solutions in the presence or absence of HPC as a cationic surfactant at pH 5.4. The Qnph–scandium(III)–HPC mixed solution shows a considerable bathochromic shift, and the absorbance is greater and stabler than that in the presence of poly(oxyethylene)sorbitan monolaurate (LT-221) as a nonionic surfactant. A maximum difference in absorbance between Qnph–scandium(III) and Qnph solutions is distinctly observed at 555 nm in the presence of HPC.

The absorbance at 555 nm is maximal and practically independent of pH in the range 4.7—5.8. Subsequent measurements were carried out pH 5.4 for determination of scandium(III).

The absorbance at 555 nm was constant when the volume of 1.0×10^{-3} mol dm^{-3} Qnph solution was varied between 1.0—2.5 cm^3. Hence 1.5 cm^3 of 1.0×10^{-3} mol dm^{-3} Qnph solution was chosen for determination of scandium(III).

HPC, HTAC, and zephiramine (Zp) as cationic surfactants were tested, and HPC showed a remarkably increasing effect on the stabilization and sensitivity. The effect of changing the concentration of HPC was studied. A maximum and constant

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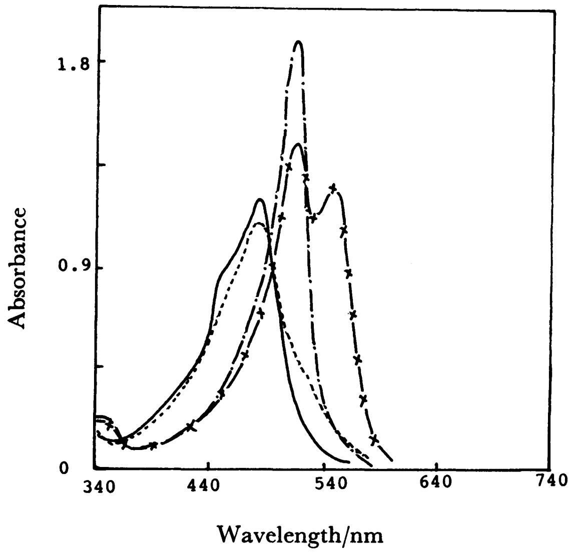

Fig. 1. Absorption spectra of scandium(III)–Qnph solution and Qnph solution in the presence and absence of HPC at pH 5.4.
Scandium(III): 1.0×10^{-5} mol dm^{-3}; Qnph: 4.0×10^{-5} mol dm^{-3}; HPC: 4.0×10^{-3} mol dm^{-3}; Reference: water; ——: Qnph solution in the presence of LT-221; ----: Qnph–scandium(III) solution in the presence of LT-221; —·—: Qnph solution in the presence of HPC; —×—: Qnph–scandium(III) solution in the presence of HPC.

Table 1. Effect of Foreign Ions

Foreign ions	Added as	Added µg	Added molar ratio	Absorbance at 555 nm	Found µg
—	—	—	—	0.414	2.7
Th(IV)	Nitrate	5.8	1/2	0.511	3.4
Fe(III)	Sulfate	2.8	1	0.504	3.3
		0.6	1/2	0.420	2.7
Al(III)	Nitrate	0.7	1/2	0.477	3.1
Ce(III)	Nitrate	350.3	50	0.936	6.1
		7.0	1	0.435	2.8
Pb(II)	Nitrate	20.7	1	0.420	2.7
		103.6	10	0.445	2.9
Cu(II)	Nitrate	1.6	1/2	0.625	4.1
Co(II)	Nitrate	294.7	100	0.420	2.7
Zn(II)	Nitrate	326.9	100	0.564	3.7
Cd(II)	Nitrate	562.1	100	0.344	2.2
Mg(II)	Chloride	121.5	100	0.414	2.7
CN^-	Potassium	13.0	10	0.354	2.3
SO_4^{2-}	Sodium	480.3	100	0.414	2.7
NO_2^-	Sodium	115.0	50	0.375	2.5
F^-	Sodium	19.0	20	0.399	2.6
PO_4^{3-}	Potassium	0.5	1/10	0.365	2.4
Citrate	Sodium	7.8	1	0.285	1.9
Oxalate	Sodium	5.3	1	0.386	2.5
Tartrate	Sodium	147.1	20	0.418	2.7
		735.5	100	0.393	2.6

Scandium(III) taken: 2.7 µg/10 cm^3: Qnph: 1.5×10^{-4} mol dm^3; HPC: 2.0×10^{-3} mol dm^3; pH: 5.4; Reference: Reagent blank.

absorbance of Qnph-scandium(III) solution against Qnph solution was observed upon addition of 1.0—4.0 cm^3 of 1.0×10^{-2} mol dm^{-3} HPC solution to the final volume of 10 cm^3. Thus, all further measurements were made with 2.0×10^{-3} mol dm^{-3} HPC as the final concentration.

A good linear relationship was observed over the range 0—4.5 µg of scandium(III) in the final volume of 10 cm^3 at 555 nm against a reagent blank. The apparent molar absorptivity is 1.0×10^5 dm^3 mol^{-1} cm^{-1}, and the Sandell sensitivity is 0.0005 µg cm^{-2}. The coefficient of variation (C.V.) for 5 replicate determinations is 0.6% for 2.7 µg of scandium(III), whereas C.V. in the presence of LT-221 is 4.5%.

The molar ratio of scandium(III) to Qnph was established by the molar-ratio and continuous-variation methods in the presence of high-concentration HPC. The results obtained indicate that the molar ratio of scandium(III) to Qnph is 2:3. On the other hand, the molar ratio of Qnph to scandium(III) in the coexistence of LT-221 is 3:2 as determined by both the molar-ratio and continuous-variation methods. Accordingly, the molar ratio of HPC to Qnph was subjected to determination by the molar-ratio method and found to be 2:1. Though further investigation is necessary, it is deduced from these results that the ternary complex formed in this reaction system may be expressed as $(Sc)_2(Qnph)_3(HPC)_6$.

Of the metal ions tested, iron(III), aluminium(III), thorium(IV), and copper(II), when each present in a small amount result in positive errors because of formation of colored complexes with Qnph in a weakly acidic medium. On the other hand, presence of iron(II), cobalt(II), or cadmium(II) causes no interference even when they are 2—50 times scandium(III) in amount, and large amounts of calcium(II) or magnesium(II) do not interfere. Though presence of citrate, oxalate, or phosphate ion results in negative errors, presence of tartrate or cyanide ion causes no interference when they are 5—20 times scandium(III). The results are summarized in Table 1.

Scandium(III) is entirely masked by addition of large amounts of sodium fluoride solution as a masking agent. On the other hand, iron(III) or aluminium(III) is little affected by addition of small amounts (for example, 3.0×10^{-3} mol dm^{-3}) of sodium fluoride solution as a masking agent. Therefore, aluminium(III) or iron(III) can be determined by measuring at 555 nm absorbances, respectively, of Qnph-aluminium(III)-scandium(III)-sodium fluoride and Qnph-aluminium(III)-scandium(III) solutions, or Qnph-iron(III)-scandium(III)-sodium fluoride and Qnph-iron(III)-scandium(III) solutions, as shown in Fig. 2.

In conclusion, a simple, rapid, and sensitive spectrophotometric determination of scandium(III) by using Qnph-scandium(III)-HPC ternary complex has been established. The calibration curve is linear

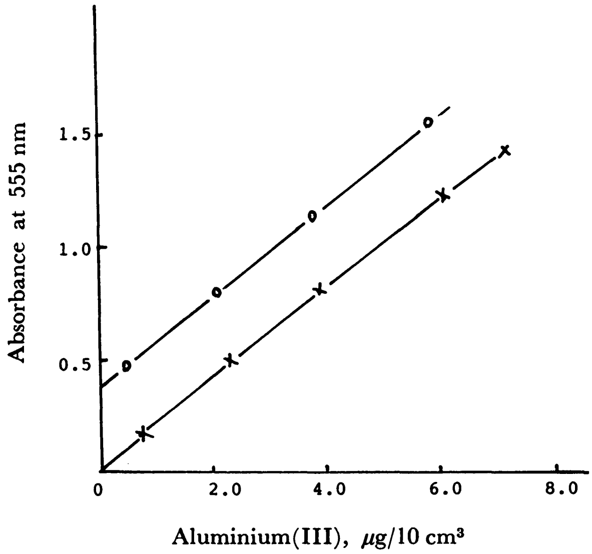

Fig. 2. Calibration curve for aluminium(III) in the presence of scandium(III) and fluoride ion. Scandium(III): 5.0×10^{-6} mol dm^{-3}; HPC: 4.0×10^{-3} mol dm^{-3}; F^{-}: 3.0×10^{-3} mol dm^{-3}; Qnph: 1.5×10^{-3} mol dm^{-3}; pH: 5.4; Reference: Reagent blank; —×—: Aluminium(III)-F^{-}-scandium(III); —∘—: Aluminium(III)-scandium(III).

in the concentration range 0—4.5 μg/10 cm^3 for scandium(III). The apparent molar absorptivity is 1.0×10^{5} dm^3 mol^{-1} cm^{-1} for scandium(III) with a Sandell sensitivity of 0.0005 μg cm^{-2} at 555 nm. The sensitivity of the proposed method is about 4—5 times as high as those of the Arsenazo III, XO, MTB, and BPR methods.[5–8]

Moreover, the proposed method using the ternary complex may be used for separative assay of aluminium(III)-scandium(III) mixture or iron(III)-scandium(III) mixture solution by use of sodium fluoride as a masking agent.

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