

Determination of Trace Scandium by Ion-Exchanger Phase Spectrophotometry with *p*-Nitrochlorophosphonazo

Chung-Gin Hsu*, Qun Xu, and Jiao-Mai Pan

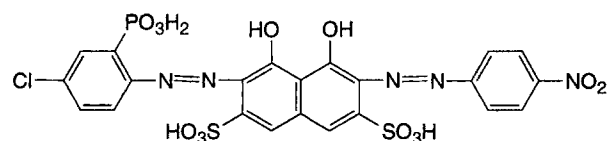
Department of Chemistry, East China Normal University, Shanghai 200062, Peoples Republic of China

Abstract. Ion-exchanger phase spectrophotometry with *p*-nitrochlorophosphonazo (CPApN) has been developed for the determination of scandium. The linear range is 1–8 µg of scandium in 50 ml of solution, using 0.8 g of resin, with an apparent molar absorptivity of $2.76 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$. Aluminum and rare earth elements in reasonable amounts do not interfere. The method has been applied successfully to the determination of scandium in alloys, with relative standard deviations of 2–4%.

Key words: ion-exchanger phase spectrophotometry, scandium determination, *p*-nitrochlorophosphonazo.

For the spectrophotometric determination of trace amounts of scandium, arsenazo III and xylenol orange have been recommended as chromogenic reagents [1], but their sensitivities are low. Recently, some asymmetric bisazo derivatives of chlorophosphonazo [2, 3] and derivatives of phenylfluorone [4] in the presence of surfactants have been proposed to give more sensitive reactions with scandium. However, their selectivities seem not to be satisfactory and prior separation is often required to determine scandium in complex samples [4].

Ion-exchanger phase spectrophotometry, suggested by Yoshimura et al. [5], has been applied to determine many ions in water samples [6, 7]. In this paper, scandium was determined by ion-exchanger phase spectrophotometry with *p*-nitrochlorophosphonazo (CPApN, Scheme I) [8] as a chromogenic reagent.



Scheme I

The proposed method is selective and sensitive due to selective sorption and concentration of scandium in the resin phase, and has been applied to determine scandium in alloy and low-alloy steel samples.

Experimental

Apparatus

Absorption spectra and absorbances were recorded and measured on a Beckman DU-7HS spectrophotometer with 5-mm cells and a model HJ-3 magnetic stirrer was used.

Reagents

Anion-exchange resin. The resin No. 717 [9] (20–40 mesh, Cl^- form) produced by Shanghai Resin Factory is a strong-base resin, equivalent to Dowex 1. The resin was washed with water several times and treated with 2 mol/l hydrochloric acid, and finally washed with water until the washings were free of chloride. The resin was then air dried and stored in a polyethylene container.

Stock standard solution of scandium (1 mg/ml). Dissolve scandium oxide (Specpure) in 6 mol/l hydrochloric acid, evaporate the solution to remove the excess of acid, and dilute with (1 + 100) hydrochloric acid to 100 ml. Dilute further to obtain a 10 µg/ml ($2.22 \times 10^{-4} \text{ mol/l}$) working standard solution.

CPApN solution (0.02%). Dissolve 20 mg of CPApN [8] in 100 ml of water.

All chemicals used were of analytical-reagent grade.

Procedures

A. General. Take a test solution containing not more than 8 µg of scandium in a 100-ml beaker, add 2 ml of 3 mol/l sulfuric acid and 3.5 ml of 0.02% CPApN solution. Dilute the solution to a volume of 50 ml with water and mix well. After standing 10 min for full color development, add 0.8 g of resin, and stir for 25 min. Withdraw the resin with a dropper and place it into a 5-mm cell, remove the excess water on the surface with the same dropper and ensure that the resin is evenly packed. Measure the difference of the absorbances at 689 and 800 nm ($\Delta A = A_{689} - A_{800}$) against a reagent blank resin (pre-

* To whom correspondence should be addressed

pared in the same manner as that for the test solution but without the addition of scandium).

B. Distribution measurements [10, 11]. Take 5 μg of scandium, add reagents and work in the same manner as above. The scandium concentration in the colored resin was determined as described in the general procedure. The aqueous phase was then treated in the same manner with a further batch of resin, and the scandium remaining in the aqueous phase was measured as before.

The distribution ratio $D = \mu\text{mol of Sc sorbed per g of resin} / \mu\text{mol of Sc per ml of solution}$ was calculated in the usual way.

C. Determination of scandium in alloys. To an appropriate amount of sample, add 10 ml of (1 + 1) aqua regia, heat to decompose the sample and evaporate to near dryness. After cooling to room temperature, dissolve the residue with water, transfer the solution to a 100-ml calibrated flask and dilute to the mark with water. Place an aliquot part of the resultant solution in a 100-ml beaker, add 1 ml of 5% ascorbic acid solution, then follow the general procedure for the determination of scandium.

Results and Discussion

Absorption Spectra

Scandium forms with CPAPN a blue complex in acidic medium [3]. Both CPAPN and the complex can be sorbed on an anion-exchange resin. As shown in Fig. 1, the maximum absorbance of CPAPN in the resin is at 560 nm (Curve 1), while the complex in the resin exhibits two absorption peaks at 635 and 689 nm (Curve 2). At the second peak (689 nm), the complex in the resin gives the highest absorbance and the absorption of the reagent blank in resin is weak. A dual-wavelength measurement of the absorbances of the

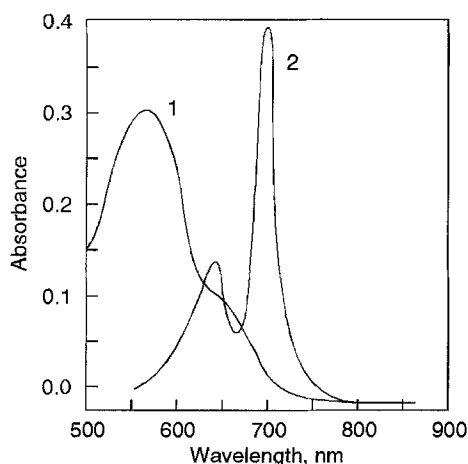


Fig. 1. Absorption spectra. 1 Reagent blank (CPAPN, 2.12×10^{-6} mol/l) in resin phase against blank resin. 2 Sc-CPAPN complex against reagent blank (in resin phase). H_2SO_4 , 0.12 mol/l; Sc, 2.22×10^{-6} mol/l; CPAPN, 1.06×10^{-5} mol/l; resin, 0.8 g; stirring time, 25 min; $l = 5$ mm

complex ($\Delta A = A_{689} - A_{800}$) is proposed to minimize the effect of the resin in all subsequent work.

Conditions for the Complex Sorption on the Resin

As shown in Fig. 2, the scandium-CPAPN complex in the resin phase gave maximal and almost constant absorbance in the range of 0.03–0.15 mol/l sulfuric acid. In this range, the distribution ratio was found to be 2.2×10^4 . Hence 0.12 mol/l was chosen for the general procedure.

The optimum concentration of CPAPN ranged from 0.91 to 1.25×10^{-5} mol/l. Higher concentrations of CPAPN led to low absorbance, due to competitive sorption between complex and reagent on the resin phase; therefore 1.06×10^{-5} mol/l CPAPN was adopted (this corresponded to 3.5 ml of 0.02% CPAPN in 50 ml of solution).

The stirring time for the sorption of the complex is shown in Fig. 3. Obviously, a time of 25 min for stirring is sufficient. The complex, once sorbed on the resin, is stable for at least 60 min.

Because the use of a large amount of resin lowers the absorbance, the optimum amounts of the resin used for filling the cells of 0.8 g in each determination.

Analytical Characteristics of the Method

A calibration graph constructed by plotting the difference of absorbances between 689 nm and 800 nm ($\Delta A_{689-800}$) versus scandium concentration was linear over the range 1–8 μg of scandium in 50 ml of solution with 0.8 g of resin. The straight line equation by least-squares treatment ($n = 8$) was $\Delta A = 0.0614 + 0.0637C$

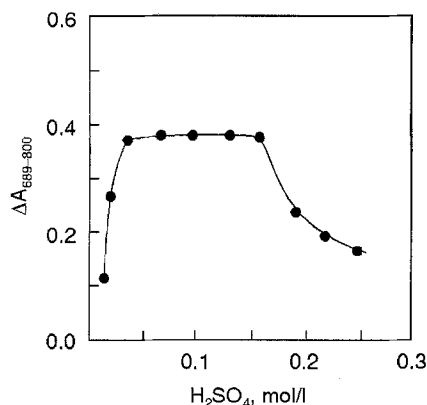


Fig. 2. Effect of concentration of sulfuric acid. Conditions as for Fig. 1 except the concentration of sulfuric acid

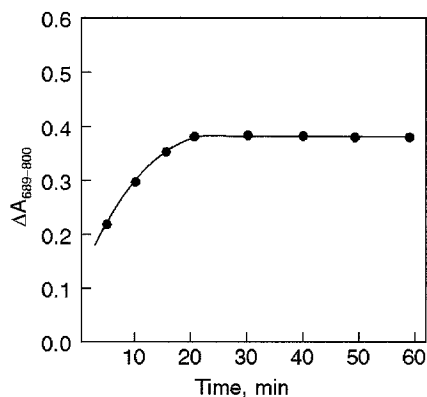


Fig. 3. Effect of stirring time. Conditions as for Fig. 1 except the stirring time

($r = 0.996$), where C is micrograms of scandium in 50 ml of solution and r is the correlation coefficient.

The apparent molar absorptivity (ϵ') and Sandell's sensitivity were calculated from increments on the slope of the calibration graph to be $2.76 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ and 0.16 ng cm^{-2} of scandium, respectively.

Ten replicate analyses of a test solution containing $2.0 \mu\text{g}$ of scandium gave a coefficient of variation of 2.2%.

Composition of the Complex

The molar composition of the scandium-CPApN complex in the resin was ascertained by the Asmus [12] and equilibrium-shift [13, 14] methods. Both methods in-

dicated that the metal-to-ligand ratio was 1:2. However, the molar compositions of the complex in 0.22 mol/l hydrochloric acid aqueous solution were reported to be 1:2 and 1:4, respectively [3].

Effect of Foreign Ions

Solutions containing $4.0 \mu\text{g}$ of scandium and various amounts of 29 possibly accompanying was ions were prepared and the general procedure was followed. The

Table 1. Tolerance limits for foreign ions in the determination of $4.0 \mu\text{g}$ of scandium (5% error)

Foreign ions	Tolerance limits (mg)
Na(I), K(I), $\text{NH}_4\text{(I)}$	40
Zn(II), Mg(II), Fe(III) ^a	10
Cu(II), Mn(II)	5
Bi(III), Co(II), Ni(II)	2
Pb(II)	1
Ca(II), Sr(II), Cr(III), V(V)	0.5
Al(III)	0.3
Cd(II)	0.2
Ti(IV)	0.05
Ce(III), Y(III)	0.03
Th(IV)	0.02
Zr(IV)	0.005
Sulfate	> 100
Ascorbic acid	50
Nitrate	> 40
Citrate	40
Tartrate	40
Phosphate	10

^a With the addition of 50 mg of ascorbic acid.

Table 2. Determination of scandium in alloys

Sample ^a	Scandium ($10^{-3}\%$)		Coefficient of variation(%)	Recovery (%)
	Content	Found ^b		
Aluminum-brass (BY1912-1)	2.42	2.37	2.78	97.9
Manganese-brass (BY1914-1)	3.20	3.28	3.45	103
Zinc alloy (47 [#])	3.11	3.05	2.88	98.0
Low-alloy steel (31-5)	2.41	2.43	4.14	101
Magnesium alloy (ZM ₅)	3.90	3.82	2.09	97.9

^a Compositions of standard samples (%): Aluminum-brass BY1912-1: Cu(57.66), Al(3.46), Ni(2.50), Fe(0.43), Pb(0.076), Bi(0.0023), Sb(0.0040), P(0.0080). Manganese-brass BY1914-1: Cu(57.09), Mn(3.23), Al(1.18), Fe(0.98), Pb(0.18), Bi(0.0017), Sb(0.0044), P(0.013). Low-alloy steel 31-5: C(0.087), Si(0.360), Mn(1.033), P(0.0123), Cr(0.033), Ni(0.350), V(0.231), Mo(0.152), Ti(0.150), Cu(0.435), Al(0.106).

^b Mean of five determinations.

tolerance limits (5% error maximum) are shown in Table 1. Most of the ions do not interfere. 10 mg amounts of zinc, magnesium, iron and 5 mg amounts of copper and manganese are tolerable. 70-fold amounts of aluminum and 7-fold amounts of rare earth elements do not interfere.

Determination of Scandium in Alloys

Synthetic samples were prepared by introducing known amounts of scandium to solutions of standard samples and samples of copper, zinc, magnesium alloys and low-alloy steel, and the scandium contents were determined by using procedure C. The results are shown in Table 2. The recoveries of scandium obtained ranged from 97.9 to 103%.

Conclusions

The present method is simple, sensitive and selective; it provides that concentration of scandium and the color development take place simultaneously. Its sensitivity ($\epsilon' = 2.76 \times 10^5$) is twelve times higher than obtained by the aqueous CPAPN method ($\epsilon' = 2.3 \times 10^4$) [3].

Under the experimental conditions employed, large amounts of zinc, magnesium, iron, copper and manganese are tolerable. 70-fold amounts of aluminum and 7-fold amounts of rare earth elements do not interfere with the determination, which is an advantage over the other published methods.

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