The Spectrophotometric Determination of Zirconium(IV) by Solvent Extraction with Trioctylphosphine Oxide and Benzophenone

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Synopsis. The colorimetric determination of zirconium(IV) was investigated by means of liquid-liquid extraction, where zirconium in a nitric-acid solution was quantitatively extracted into molten TOPO–benzophenone at about 60 °C. The organic phase solidifies on cooling and is separated and dissolved in methanol. The addition of an ethanolic solution of 1-(2-pyridylazo)-2-naphthol to this solution yields as intense red colour.

Recently, spectrophotometric determination has again, because, with it one is able easily, come to be of interest to determine a number of metals without difficulty. However, one of the major problems is the lack of the specificities of any chromogenic agents except bathophenanthroline, 1,10-phenanthroline, *etc.* On the other hand, tributyl phosphate (TBP), tributylphosphine oxide (TBPO), and trioctylphosphine oxide (TOPO) are well known as selective extractants.[1-4] Also, solvent extraction by using naphthalene or benzophenone has the disadvantage that it must be carried out at a comparatively high temperature (70 °C), but it has the merit that metal ions can be extracted with less volume than when a liquid solvent is used, for, upon cooling, the organic phase separates out as a solid.[5-8]

In this investigation, we studied the selective spectrophotometric determination method of zirconium, combined with such a selective extraction and a conventional colour development.[9]

Experimental

Reagents and Apparatus. All the reagents were of an analytical grade. The standard zirconium(IV) solution was prepared by dissolving 0.2767 g of zirconium nitrate in ion-exchanged water and by then diluting the solution to 100 cm^3. Stock solutions of the other metal salts were prepared by dissolving salts in 0.1 mol dm^{-3} hydrochloric acid or nitric acid. The trioctylphosphine oxide (TOPO), tributylphosphine oxide (TBPO), tris(2-ethylhexyl)-phosphine oxide (TEHPO), and triphenylphosphine oxide (TPPO) were used without further purification. The absorbancy curves of the solution contained in a 1-cm matched-glass cell were measured with a Hitachi 101 spectrophometer.

Procedure. Transfer a solution containing 0—230 μg of zirconium into a 100-cm^3 Erlenmeyer flask with a tight-fitting stopper, and adjust the acidity of the solution to 2 mol dm^{-3} with nitric acid. Add 100 mg of TOPO and 300 mg of benzophenone. Heat the flask on a water bath at about 60 °C untile the TOPO phase melts completely, and then shake it vigorously for 2 min. Remove the flask from the bath, cool the molten extractant rapidly while stirring in cold water, and separate the resulting solidified extract in granular form from the aqueous solution by filtration. Wash the extract several times with water and transfer it to a 10-cm^3 volumetric flask containing 1 cm^3 of a 1-(2-pyridylazo)-2-naphthol (PAN) solution and 0.5 cm^3 of a triethanolamine solution. Dilute the solution to the mark with methanol. Shake well and measure the absorbance of the solution at 545 nm against a reagent blank.

Results and Discussion

Extraction with Various Extractants. The extraction was carried out through the procedures using TOPO, TBPO, TEHPO, and TPPO. TOPO and TBPO would seem to be suitable extractants. However, TBPO interferes with the colour development of zirconium with PAN. Therefore, we used TOPO as an extractant in the following experiments. Also, we simultaneously examined the effect of acidity on the extraction. Zirconium was extracted quantitatively from more than 2 mol dm^{-3} nitric acid. Its extractability from a hydrochloric-acid solution is not so much as that from a nitric-acid solution; for instance, the extraction percentage in a 2 mol dm^{-3} nitric-acid medium showed more than 99%, while that at hydrochloric acid reached only 55% at 50 °C, though it increases with an increase in the temperature and, at 80 °C, reaches 99%.

Effect of Amount of TOPO. The experiments were carried out at temperatures ranging from 50 to 90 °C in order to examine the relation between the amount of TOPO and the extraction percentage. It was found that the elevation of the extraction temperature causes the extractability to increase slightly, and that adding more than 100 mg of TOPO brings to about a quantitative extraction. Further, naphthalene and biphenyl were investigated as diluents instead of benzophenone; however, naphthalene is not sufficiently soluble in methanol, and so it interferes with the colour developing because of forming a opaque solution.

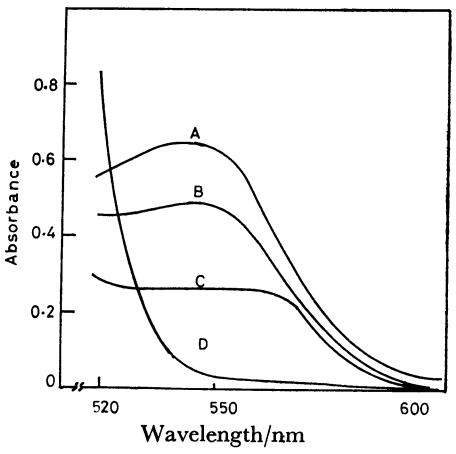

Fig. 1. Absorption curves.
A: 4.6 ppm Zr(IV) *vs.* reagent blank (TOPO), B: 4.6 ppm Zr(IV) *vs.* reagent blank (TBPO), C: 4.6 ppm Zr(IV) *vs.* reagent blank (TEHPO), D: reagent blank *vs.* ethanol, PAN: 1.0 cm^3, buffer: 0.5 cm^3.

Absorption Spectra. Figure 1 show the absorption spectra of the reagent blank and of the PAN–zirconium-(IV) complex in a benzophenone–methanol solution resulting from taking in 46 μg of zirconium through the above procedures. The magnitudes of the absorbance are in this order: TOPO, TBPO, and TEHPO; this order is compatible with that of the extraction percentage. However, no quantitative relation was observed between these values. For instance, the TBPO complex is as extractable as the TOPO one, but the absorbance of the former is only two-thirds that of the latter. We may suppose that TBPO complex is more stable than the TOPO complex; therfore, the exchange reaction does not proceed not so much as in the TOPO complex. Further, we examined how the absorbance varied as a function of the amount of triethanolamine or PAN added. The addition of 0.5 cm^3 of 10% triethanolamine as a buffer sufficed to develop the colour of the zirconium complex. Also, the colour intensity showed a plateau. Adding a large amount of a PAN solution causes the reagent blank to have a colour of a strong intensity. Therefore, the determination was carried out by adding 1 cm^3 of a 0.1% PAN solution to 10 cm^3 of a zirconium solution.

Choice of Solvent. Tests were made with verious solvents in dissolving mixtures of the complex and benzophenone. Such a mixture is soluble in many organic solvents, such as methanol, ethanol, *N,N'*-dimethylformamide, and acetone, but dissolving with cyclohexane, isobutyl methyl ketone, and chloroform formed an opaque solution. Furthermore, to these solutions are also added 1 cm^3 of a 0.1% PAN solution. The spectra observed are shown in Fig. 2. The absorbance is higher in methanol than in the others.

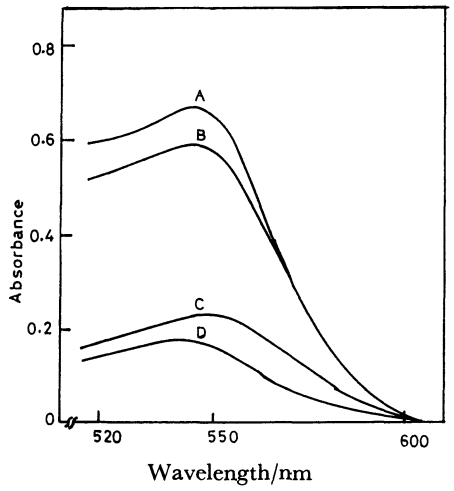

Fig. 2. Effect of the various solvents.
A: CH_3OH, B: C_2H_5OH, C: DMF, D: $(CH_3)_2CO$.
Conditions Zr(IV): 4.6 ppm, PAN: 1.0 cm^3, buffer: 0.5 cm^3, TOPO: 100 mg, benzophenone: 300 mg.

Effects of Diverse Ions. Possible interference was looked for by placing 46 μg of zirconium in 25 cm^3 of a 2 mol dm^{-3} nitric-acid solution. One milligram of the following cations gave no interference; Mg(II), Ca(II), Sr(II), Ba(II), Y(III), La(III), Ce(III), Nd(III), Cr(III), Mn(II), Cu(II), Zn(II), Al(III), Fe(III), V(V), Co(II), and Ni(II), but Sc(III) and U(VI) gave considerable positive interference. As has been mentioned above, the apparent molecular absorptivity, 1.24×10^4 cm^3 mol cm^{-1}, we obtained is not so large as that[10] obtained by combining with the colour development and the solvent extraction with dibutyl hydrogenphosphate. However, zirconium can be determined up to 10^{-5} mol dm^{-3}, as it can be easily concentrated two hundred times by means of the proposed extraction, though allowance must be made for large volumes by shaking for a longer times and by using larger amounts of the extractants.

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