A Rapid, Selective and Sensitive Spectrophotometric Method for Determination of Cerium(IV)

BIJOLI K. PAL*, BIRENDRA K. MITRA and SATI P. DAS THAKUR

Department of Chemistry, Jadavpur University, Calcutta-700 032

A better selective, sensitive, simple and rapid chloroform extractive spectrophotometric method for the determination of cerium(IV) using o-iodobenzoyl-o-tolylhydroxylamine (OIBOTHA) has been developed. The colour system of Ce^{IV} – OIBOTHA, extracted from ammoniacal medium, in the presence of ᴀ-picoline, obeys Beer's law at λ_{max} 450 nm for 0.40 – 32 ppm of Ce^{IV}, the optimum concentration range being 1.5 – 30 ppm. The percentage relative error is 2.65% according to Ayer's equation, the molar absorptivity 5.744×10^3 dm^3 mol^{-1} cm^{-1} and the Sandell sensitivity for an absorbance of 0.001 is 0.0244 μg cm^{-2}. The stoichiometric composition of the complex is found to be 1 : 4 (metal – ligand). Over forty cations and anions do not interfere. The method has been tested on few synthetic samples containing cerium(IV) and the results are encouraging.

ANALYTICALLY, cerium in its tetravalent state differs significantly from the rest of the 'lanthanides' due to its immense oxidising power in acid solutions. This property of cerium(IV) stands on the way of its determination by using organic reagents in most cases Perhaps, this is the principal reason which restricts its spectrophotometric determination procedure. Only a few dyes[1,2] and mixed-ligands[3,4] which could withstand the oxidative reaction of cerium(IV) to some extent, are capable of forming coloured complex with the metal ion of meaningful sensitivity, but the methods suffer from lack of selectivity, instability of the colour system and having increasing complexity, narrower pH range and prolong time factor. As ceric cerium has the inherent oxidative menacing role upon the tender constituent, like cell, body fluid, enzymes etc. of living beings and with the advent of atomic energy programmes using thorium extracted from ores like monazite, a common ore for cerium as well, the presence of cerium(IV) in the environment proves alarming. This necessitates its determination by simpler and rapid way of spectrophotometry, and one such method has been described here.

Experimental

Uv spectra were recorded on a Hilger spectrophotometer with 1 cm glass cells, and pH measured with a Elico pH meter.

ᴀ-Picoline (A.R.) was freshly distilled. Chloroform used was freed from alcohol and other impurities by the treatment of concentrated sulphuric acid followed by successive washing with ammonia solution, then distilled and dried over anhydrous sodium sulphate.

The reagent, OIBOTHA, was prepared according to the method described earlier[5] and a 0.6% solution in acetic acid was used. A standard stock solution

of cerium(IV) was prepared by dissolving ammonium tetrasulphato cerate (Proanalysis, E. Merck) in tripple-distilled water containing concentraed sulphuric acid (few ml) and standardised[6]. Standard solutions of Nb, Ta, Zr and Hf were prepared[7], using the oxides of the metals (Specpure, Johnson-Matthey). Solutions of diverse ions were prepared from their soluble salts. Hydrolysable salts like those of bismuth, antimony etc. were treated with complexing agent like tartrate to prevent hydrolysis.

All the chemicals used were of A.R. grades and water used was tripple-distilled.

General procedure : To a solution (5 ml) containing 4 – 320 μg of cerium(IV) in a 100 ml separating funnel were added freshly distilled ᴀ-picoline (2 ml) and a 0.6% reagent solution (7 ml) and then diluted to about twice its volume with water and made strongly ammoniacal by adding liquor ammonia. The solution was then allowed to stand for 5 min and extracted with chloroform (3 ml+2× 2 ml). The organic phase was dried (anhydrous sodium sulphate), transferred to a 10 ml volumetric flask and the volume made up with chloroform. The absorbance was measured against reagent blank at 450 nm.

Results and Discussion

Factors affecting the absorbance : Effect of pH revealed that the formation of the chelate and extraction are complete in the pH range 5 – 11 but the extraction time is much less in the pH range 8.5 – 11. As it is very convenient to make the solution ammoniacal, this condition is much preferred. It was observed that if the aqueous system contains little ᴀ-picoline, then the extraction time could be reduced further. 2 – 3 ml of ᴀ-picoline was found to be sufficient for the recommended range (4 – 320 μg/10 ml) of Ce^{IV} concentrations ; it simply

helps the extraction. Addition of 6–10 ml of a 0.6% reagent solution was found to produce a constant absorbance upon a fixed metal concentration range of 0.4–32 0 ppm. The wine red Ce^{IV}–OIBOTHA chelate extracted iñ chloroform is found to be stable even upto 3 h after extraction ; the effect of longer time was not studied.

Physical constants of complex :

Absorption spectra : Solutions were prepared containing the ligand and cerium(IV) solution in different concentrations and pH conditions, the total volume of extracting solvent (chloroform) being maintained at 10 ml in each case. In all cases the wavelength of the maximum absorbance was found at 450 nm and also at 490 nm, but because the former value lies in the region of a plateau, all the subsequent measurements were made at this wavelength. The same characteristic spectrum was obtained in the presence or absence of ∝-picoline without any appreciable alteration of the absorbance suggesting the formation of a single complex.

Beer's law, sensitivity, molar absorptivity and photometric error : The colour system obeys Beer's law in the range 0.40–32 ppm of Ce^{IV} concentrations. The optimum range evaluated from Ringbom's curve is 1.5–30 ppm of Ce^{IV}. The Sandell sensitivity for an absorbance of 0.001 is 0.0244 μg cm^{-2}. The molar absorptivity is 5.744×10^3 dm^3 mol^{-1} cm^{-1}. The relative error per 1% photometric error is 2.65% according to Ayers' equation.

Composition of complex : The stoichiometric composition investigated by both Job's method and mole-ratio method suggested that the metal–reagent is 1 : 4.

Effect of diverse ions : The following inorganic ions and organic complexing agents do not interfere in the determination of 12 ppm of Ce^{IV} (values shown in parenthesis are concentration in ppm studied and not maximum tolerance limit unless specified) : $Co^{II}(200)$, $Ni^{II}(200)$, $Cu^{II}(200)$, $Cd(100)$, $Hg^{II}(100)$, $Mg(200)$, $Ca(150)$, $Be(200)$, $Mn^{II}(200)$, $Al(200)$, $Cr^{III}(200)$, $Cr^{VI}(50)$, $Mo^{VI}(50)$, $W^{VI}(100)$, $U^{VI}(100)$, $Sn^{IV}(200)$, $Zr(100)$, $Hf(100)$, $Nb^{VI}(100)$, $Ta^{V}(100)$, $V^{V}(200)$, alkali metals (10000 each), Cl^- (10000), F^- (5000), suphate (10000), thiosulphate (200), nitrate (10000), tartrate (7000), citrate (5000) and oxalate (1000). However, Fe^{II}, Fe^{III}, EDTA and strong reducing agents interfere strongly. The interference from Fe^{III} was removed by the extraction of its anionic (chloro) complex with ether from strongly hydrochloric acid solutions of the sample mixture before the reagent addition. The use of a mixture of tartaric acid (50 mg) and citric acid (5 mg) has been found to have an effective masking action on a large number of foreign metal ions.

Analysis of synthetic mixtures :

Few synthetic mixtures of varying compositions containing cerium(IV) and diverse ions of known concentrations were by the present method using tartaric–citric acid mixtures as masking agents, and the results were found to be reproducible and satisfactory.

Acknowledgement

References

1. H PODFIGURNA and D. ZIMUA, *Rozpr. Wyds.*, 1973, 9, 1977.
2. A. I. KIRILLOV, L. P. SHANLINA and N. A. VLASSOV, *Khim. Technol*, 1975, 18, 551.
3. A. I. KIRILLOV, L. A. TURKINA and N. A. VLASSOV, *Khim. Technol.*, 1974, 17, 1291.
4. A. I. KIRILLOV, L. A. TURKINA and N. A. VLASSOV, *Khim. Technol.*, 1975, 18, 381.
5. B. K. PAL, S. P. DAS THAKUR and B. K. MITRA, *Talanta*, 1980, 27, 754.
6. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis", 3rd. ed, Longman, London, 1972, p. 317.
7. B. K. PAL and B. CHOUDHURY, *Mikrochim. Acta*, 1984, 2, 121.