SPECTROPHOTOMETRIC DETERMINATION OF TRIVALENT CERIUM WITH FERRIIN IN THE PRESENCE OF TETRAVALENT CERIUM

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A method is suggested for the indirect determination of cerium(III) ions in the presence of a high excess of tetravalent cerium. Ce(III) is oxidized to Ce(IV) by tris(1,10-phenanthroline)iron(III) complex (ferriin) in the presence of sodium diphosphate, and the purple-red iron(II) complex (ferroin) formed is determined photometrically at 530 nm. Trivalent cerium can be so determined in quantities of 0—400 µg/50 ml with a relative error of $\pm 3 \cdot 5\%$. Cerium(III) was determined in commercial cerium(IV) sulphate and cerium dioxide preparations.

A number of methods have been developed for the photometric determination of trivalent cerium in aqueous solutions based on the formation of colour chelates[1,2]. These methods, however, are unsuitable for systems containing also cerium(IV) ions because the organic ligands in acid solutions are oxidized by them. In concentrations higher than $0 \cdot 5$ mmol 1^{-1}, cerium(III) ions in the presence of tetravalent cerium can be determined indirectly after their oxidation with permanganate in acid solutions[3,4]. The measurement of the absorption bands of cerium(III) and cerium(IV) in the UV region, however, only suits to equimolar solutions of the two valency forms.

Cerium(IV) can be determined based on the oxidation of tris-phenanthroline iron(II) complex (ferroin) in acid solutions[5,6], and this approach can be applied also to the determination of cerium in both oxidation states if trivalent cerium is additionally oxidized and the analysis is repeated; again, however, the two valency forms should be present in approximately equal proportions. A method for the determination of cerium(III) by its oxidation by the di-µ-hydroxo-bis/bis(phenanthroline)/iron(III) complex cation in neutral solutions under the action of UV radiation has also been suggested[7].

The present work is devoted to the photometric determination of cerium(III) ions in the presence of cerium(IV) ions in an excess of several orders of magnitude, particularly from small amounts of sample. A method is developed based on the oxidation of cerium(III) with ferriin in neutral or weakly basic solutions while

masking tetravalent cerium with alkali diphosphate. The colour intensity of the ferroin formed is measured at 530 nm.

EXPERIMENTAL

Chemicals and Apparatus

Cerium(III) sulphate solution was obtained by dissolving the octahydrate of reagent grade purity in 100 ml of water containing 0·5 ml of HCl (1 : 1) so that 1 ml of solution contained 0·5 mg of cerium.

The photometric measurements were carried out on a Pulfrich photometer with an Elpho equipment and on a Spekol instrument with an Ek5Aut attachment (Carl Zeiss, Jena) interfaced to a K 201 recorder. The absorption spectra were measured on a Specord UV-VIS spectrophotometer (Carl Zeiss, Jena). The pH values were measured with an OP-8083 (combined electrode interfaced to an OP-208 digital pH-meter (Radelkis, Budapest).

Preparation of Reagent

Ferriin is prepared by oxidation of ferroin with chlorine gas. $(NH_4)_2Fe(SO_4)_2.6 H_2O$ (120 mg) and 1,10-phenanthroline (140 mg) are dissolved in water with an addition of 3 ml of HCl (1 : 1) and the solution is diluted to volume (100 ml). Chlorine gas is fed into 50 ml of this solution in a beaker until blue colour appears, and ferroin is then added portionwise until the blue solution of ferriin acquires a blue-red shade. The reaction is slow, and so the ferroin portions have to be added in approximately 5 min intervals. The removal of the excess chlorine is necessary because free chlorine, or hypochlorite, in alkaline solutions interferes with the procedure. The final red-blue colour is converted back with 2—3 drops of the blue ferriin solution, and the solution is allowed to stand on daylight, whereupon the colour changes again to a slight red-blue tint. The ferriin solution so obtained is used immediately for the analysis.

Procedure

The cerium(IV) salt sample is added to 20 ml of distilled water and 8 ml of saturated solution of sodium disulphate, and the pH is adjusted with ammonia to 8·5. The solution is transferred to a 50 ml volumetric flask, 3 ml of fresh ferriin solution is added, the whole is agitated, diluted to the mark with water, and agitated again. In 5 min, the light absorption at 530 nm is measured in 2 cm cells (for Ce(III) concentrations up to 400 µg/50 ml) or in 5 cm cells (for Ce(III) concentrations up to 100 µg/50 ml) against a blank. Solutions containing Ce(III) in concentrations higher than 400 µg/50 ml have to be diluted prior to the analysis. The concentrations of trivalent cerium are read from calibration graphs plotted for the regions of 0—400 and 0—100 µg Ce(III)/ /50 ml.

RESULTS AND DISCUSSION

The optimum conditions were sought for the determination of small amounts of trivalent cerium in the presence of a high excess of tetravalent cerium.

The time stability of the reagent solution is documented by Fig. 1. The effect of pH on the colour intensity of the ferroin formed by the reduction of ferriin by ce-
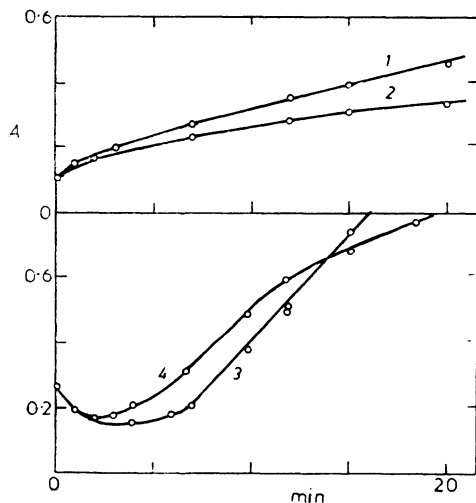
FIG. 1

Time instability of the reagent (ferriin) in 0·2M-HCl (1, 2) and 0·4M-H$_2$SO$_4$ (3, 4) solutions kept in daylight (1, 3) and in darkness (2, 4). Ferriin concentration 4 mmol l^{-1}, λ 530 nm, cell 1 cm
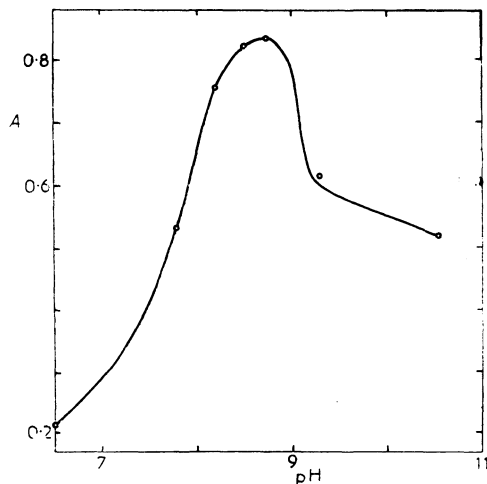

FIG. 2

Dependence of absorbance of the ferroin formed by reduction of ferriin by cerium(III) ions on pH. $c_{Na_4P_2O_7} = 15$ mmol l^{-1}, $c_{Ce(III)} = 28·5$ μmol l^{-1}, $c_{Ce(IV)} = 5$ mmol . . l^{-1}, $c_{ferriin} = 4$ mmol l^{-1}; cell 2 cm, λ 530 nm
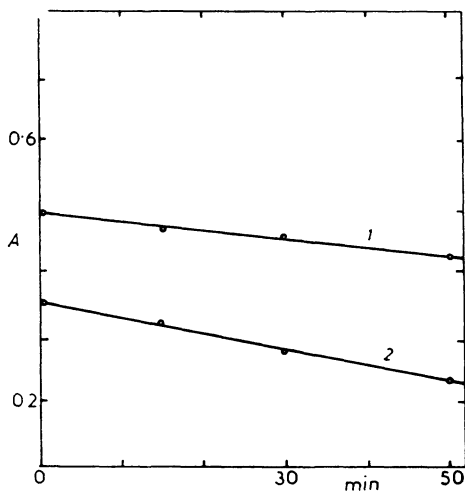

FIG. 3

Time dependence of absorbance of the ferroin formed by reduction of ferriin by cerium(III) ions. $c_{Ce(III)} = 28·5$ μmol . . l^{-1}, $c_{Ce(IV)} = 5$ mmol l^{-1}, $c_{Na_4P_2O_7} = 15$ mmol l^{-1}, $c_{ferriin} = 4$ mmol l^{-1}; cell 2 cm, λ 530 nm. 1 pH 8·5, 2 pH 10

rium(III) is shown in Fig. 2, the time dependence of the absorbance at pH 8·5 and 10 is shown in Fig. 3.

The results demonstrate that the method is applicable to the determination of cerium(III) in a minimum concentration of 0·2 mg l^{-1} in the presence of a 1 500-fold excess of tetravalent cerium. The solutions of the samples are clear, colourless, free of insoluble hydrolysis products. The colour developed is steady even with diphosphate present in concentrations as high as 25 mmol l^{-1}.

Iron(III) ions form a strong complex with diphosphate, and as a consequence, excess ferriin decomposes rapidly on its addition. Therefore, ferriin must be added quickly to the solution analyzed, by blowing the pipette for instance. In solutions at pH > 6·5 the absorbance of ferroin decreases only slowly with time (10% in 15 min) but in more acidic solutions the colour vanishes rapidly because of the back-oxidation of the ferroin by cerium(IV) ions.

The effect of dissolved oxygen must also be taken into account. While the redox potential of the Ce(IV)/Ce(III) system in acid solutions is rather high, its decrease to $E^0 = 0·34$ V in basic solutions[8,9] and to $E^0 = 0·063$ V in carbonate solutions[10] where complex formation takes place renders this system appreciably reducing. As our experiments indicate, the effect of oxygen can be neglected in solutions with pH < 8·6 but it is quite marked at pH > 9. The method in question therefore cannot be applied to oxygen-containing systems adjusted at pH > 8·6 before the addition of ferriin. Oxidizable ions such as Mn^{2+}, Co^{2+}, tellurate, free chlorine, or hypochlorite interfere over the entire pH region.

TABLE I

Results of determination of Ce(III) in cerium(IV) compounds

Chemical	Ce(III) found, %	
	photometrically	titrimetrically
Ce(SO$_4$)$_2$ *purum*	0·87	
Lachema, Brno	0·85	0·83
CeO$_2$ *purum*	1·33	
Lachema-Chemapol	1·37	1·45
Ce(SO$_4$)$_2$ Tabletten Patinal	0·64	
Merck, Darmstadt	0·65	0·61
	0·62	
	0·65	

Table I presents the results of determination of cerium(III) in cerium dioxide and cerium(IV) sulphate chemicals of various origin. The samples were analyzed photometrically by the procedure suggested and also volumetrically by titration with iron(II) salt after oxidizing cerium(III) with ammonium peroxodisulphate in the presence of silver ions as catalyst. The titrimetric analyses were repeated five times using sample weights of about 0·8 g. The relative confidence interval of the titrimetric determination as found by the Dean–Dixon test[11] was ±6%. The results of the photometric and titrimetric analyses are in a good mutual agreement. Nine replicate photometric determinations were carried out on samples containing 200 µg Ce(III) and 0·1 g Ce(IV) in 50 ml of solution. The relative confidence interval was ±3·5%.

The method was also applied successfully to the monitoring of the photoreduction of cerium(IV) under the action of UV radiation in solutions in 0·1M sulphuric acid.

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