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Extraction and Spectrophotometric Determination of Cerium(IV) with *N*-*p*-Chlorophenylcinnamohydroxamic Acid

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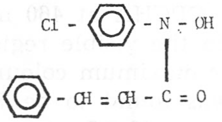
N-*p*-Chlorophenylcinnamohydroxamic acid reacts with cerium(IV) to form an orange coloured complex, quantitatively extractable into chloroform from alkaline medium. On the basis of this sensitive colour reaction, a new method for the extraction and spectrophotometric determination of cerium(IV) has been developed. The effects of foreign ions and several experimental variables on the extraction and determination of cerium(IV) have been studied and the method has been found to be simple, precise, selective, and free from the rigid control of experimental variables. The composition of the complex has been determined and the method has been found to be comparable with other methods for the determination of cerium.

N-Phenylbenzohydroxamic acid[1,2] and its analogues[3] have been reported for the extraction and spectrophotometric determination of cerium. However, these reagents are only fairly sensitive and suffer from serious interference by many common ions. It has been reported in the literature[4] that the introduction of a chloro-group into the *p*-position of the *N*-phenyl ring of hydroxamic acid increases the sensitivity of the reagent for cerium(IV). The sensitivity of the reagent can be further increased by the introduction of an additional chromophore in conjugation with the carbonyl group in the hydroxamic acid molecule. Hence, the reaction of *N*-*p*-chlorophenylcinnamohydroxamic acid, *I*, with cerium(IV) has been studied in order to improve the sensitivity as well as the selectivity of the method. On the basis of these studies a highly sensitive and quite selective method has been developed for the extraction and spectrophotometric determination of cerium(IV).



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The present paper discuss the conditions for the extraction and spectrophotometric determination of cerium(IV) with *N*-*p*-chlorophenylcinnamohydroxamic acid, CPCHA, which leads to the development of a new method for the determination of cerium.

EXPERIMENTAL

Apparatus. — A Beckman$^{(R)}$ Model 24 UV-VIS Spectrophotometer equipped with matched 1-cm quartz cells was used for absorbance measurements. A Beckman CHEM MATE pH meter was used for measurements of pH.

Standard Cerium(IV) Solution. — A stock solution of cerium(IV) was prepared by dissolving analytical grade cerium(IV) ammonium sulphate in 5% (*v*/*v*) sulphuric acid. The solution was standardized gravimetrically by the precipitation of cerium as hydroxide and ignition to cerium(IV) oxide at 800—850 °C.

Reagent Solution. — The reagent, CPCHA, was prepared by the reported method, m. p. 187 °C, literature value[5] 187 °C. A 0.2% (w/v) solution of the reagent in ethanol was used for experimental work. This solution was stable for several days.

All other reagents and chemicals used were of analytical reagent grade.

General Procedure. — An aliquot of the solution containing 0.05—0.50 mg of cerium(IV) was transferred into a 100-ml beaker and diluted to 20 ml. To the solution was transferred to a 100-ml separatory funnel after being stirred occassionally nitrate solution were added, the pH was adjusted to between 8 and 9 using ammonia and hydrochloric acid and the volume of the solution adjusted to about 50 ml. The solution was transferred to a 100-ml separatory funnel after being stirred occasionally over 30 minutes. The beaker was washed twice with 5 ml of chloroform and the washings were added to the funnel. The mixture was equilibrated for 2 minutes and allowed to separate into two phases. The chloroform phase was separated and dried over anhydrous sodium sulphate in a 50-ml beaker. The aqueous phase was washed twice with a few ml of chloroform and the washings were added to the contents of the beaker. The dried chloroform extract was transferred into a 25-ml volumetric flask and diluted to volume with chloroform. The absorbance of the coloured extract was measured at 460 nm against chloroform as blank.

For calibration, 0.5, 1.0, 2.0, 3.0, 4.0 and 4.5 ml of standard solution (0.10 mg Ce ml^{-1}) were taken according to the general procedure.

RESULTS AND DISCUSSION

Investigation of Conditions for Extraction of Cerium(IV)

Several organic solvents such as chloroform, carbon tetrachloride, 1,2-dichlorobenzene, benzene, toluene, and *o*-xylene were found to extract the cerium(IV)-CPCHA complex from the aqueous phase. The absorption spectra of the complex extracted into various solvents were found to be similar in all nonpolar solvents. However, slight changes in the absorbance values were noticed with different solvents. Chloroform was found to be the most suitable solvent for the extraction because with it the quantitative extraction of the cerium(IV)-CPCHA complex from the aqueous phase is readily accomplished.

The chloroform solution of the reagent showed a broad absorption band around 290 nm and negligible absorption in the region 400—700 nm. The chloroform extract of the complex showed an absorption maximum at 460 nm. Thus the reagent and the cerium(IV)-CPCHA complex have well separated absorption bands so that the reagent does not interfere in the photometric determination of cerium(IV) with CPCHA at 460 nm. The absorption spectra of the reagent and the complex in the visible region are shown in Figure 1.

The optimum range of pH for maximum colour development and quantitative extraction of cerium(IV) was found to be 7.5—9.5. Below pH 7.5 the extraction was incomplete and above pH 9.5 an unextractable precipitate was observed in the aqueous phase.

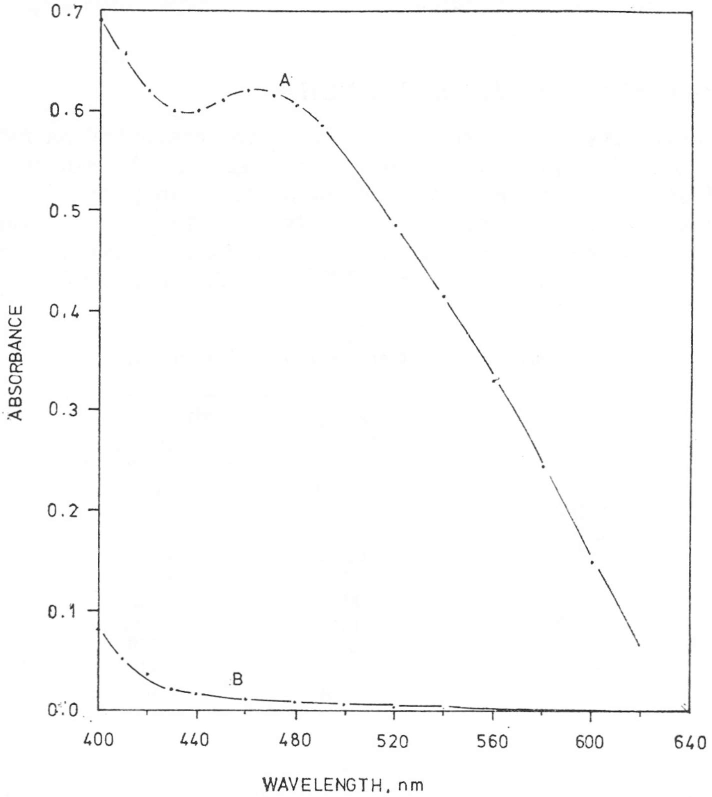

Figure 1. Absorption spectra of (A) cerium(IV)-CPCHA complex ($C_{Ce} = 8.6 \times 10^{-5}$ M + $C_{CPCHA} = 1.5 \times 10^{-3}$ M) and (B) CPCHA, the reagent ($C_{CPCHA} = 1.5 \times 10^{-3}$ M) in chloroform.

A 1 : 10 molar ratio of cerium to reagent was adequate for the complete extraction of cerium(IV). An excess of the reagent up to 100-fold molar excess has no effect on the absorbance value or on the wavelength of maximum absorption of the complex. As the reagent is insoluble in water, it was added as an ethanolic solution. It has been found that an excess of ethanol of more than 40% (*v*/*v*) in the aqueous phase tends to reduce the extraction of the cerium(IV)-CPCHA complex due to the increasing solubility. In general the volume of the aqueous phase was adjusted to 50 ml before the extraction so that the amount of ethanol should not exceed more than 20% (*v*/*v*) in the aqueous phase.

The volume of the aqueous phase can vary from 25 to 100 ml relative to a fixed volume of 25 ml of chloroform without any adverse effect on extraction efficiency or absorbance value of the chloroform extract. Variation in the temperature of the aqueous phase between 20 and 40 °C did not produce any measurable change in the absorbance of the coloured chloroform extract. The ionic strength of the aqueous phase can also be varied between 0.01 and 0.50 M with respect to ammonium nitrate and potassium chloride.

Extraction of the cerium(IV)-CPCHA complex into chloroform from the aqueous phase was found to be complete within 2 minutes. The chloroform extract of the complex was stable for a least 15 days when kept in a cool and dark place.

Determination of Cerium(IV) with CPCHA

The coloured system obeyed Beer's law in the concentration range 2—18 ppm of cerium. The optimum concentration range for the determination as evaluated from Ringbom's plot[6] was found to be 4—16 ppm of cerium. The molar absorptivity and photometric sensitivity[7] were found to be 7200 m mol^{-1} cm^{-1} and 0.019 μg of cerium per cm^2 at 460 nm respectively. Some of the results of the determination of cerium with CPCHA are given in Table I.

TABLE I

Determination of Cerium(IV) with CPCHA

Cerium taken mg	Absorbance[a] at 460 nm	Cerium found mg
0.050	0.105	0.051
0.100	0.206	0.100
0.150	0.304	0.148
0.200	0.410	0.199
0.250	0.515	0.250
0.300	0.622	0.302
0.350	0.720	0.350
0.400	0.818	0.398
0.450	0.923	0.449
0.500	1.036	0.504

[a] Measured after diluting the chloroform extract to 25 ml.

The precision of the method was evaluated from the measurements of ten samples each containing 0.2 mg of cerium in 25 ml of solution and the relative standard deviation was found to be ±0.5%. The results of the precision estimation are given in Table II.

TABLE II

Data for Precision Estimation of the Method

Cerium taken mg	Cerium found mg	Mean value mg	Number of measurement	Standard deviation
0.200	0.200	0.200	10	±0.001
	0.201			
	0.200			
	0.198			
	0.200			
	0.200			
	0.199			
	0.200			
	0.202			
	0.200			

The effect of other ions on the determination of cerium(IV) with CPCHA was studied by adding a known quantity of the ion in question to a solution containing 0.2 mg of cerium. An excess amount of the reagent was added and the cerium content of the solution was extracted and determined by following the general procedure described earlier.

Several metal ions form coloured complexes with the reagent and interfere seriously with the determination of cerium(IV). However, the interferences due to many metal ions were eliminated by adopting a two stage extraction procedure for the determination of cerium. Fe(III), Ti(IV), Zr(IV), Hf (IV), V(V), Nb(V), Ta (V), and U(VI) were separated from cerium(IV) by extraction with the chloroform solution of the reagent in the pH range 1—3 or even at a lower pH. Cerium(IV), remains in the aqueous phase under these conditions, was extracted and determined after raising the pH of the aqueous phase to 8.5.

The tolerance limits of the other ions taken as the concentration (ppm) causing an error of less than 2% are given in parentheses.

The tolerance limits in the determination of 10 ppm of cerium for alkali metal ions (1000); Ca^{2+}, Sr^{2+}, Ba^{+2}, Mg^{2+} (200); Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Tl^{+} (200); Th(IV), lanthanide (100); Mo(VI), W(IV), (100); Fe(III), Ti(IV), Zr(IV), Hf(IV), V(V), Nb(V), Ta(V), U(VI) (200); acetate, carbonate, chloride, nitrate, oxalate, sulphate (1000); citrate, tartrate (200). Cu^{2+}, Ni^{2+}, Co^{2+}, fluoride and phosphate interfere at all levels.

Thus most of the ions normally associated with cerium in ores and complex materials do not interfere in the determination of cerium(IV) with CPCHA and the method is quite selective.

Comparison with Other Methods

The present method has been compared with the well known conventional methods[8–17] recommended for the spectrophotometric determination of cerium. The details such as name of the reagent, colour of the complex, wavelength of maximum absorption and photometric sensitivity are summarized in Table

TABLE III

Comparison with Other Methods

Method or Reagent	Colour of complex	λ max nm	Sensitivity μg Ce cm^{-2}	Reference
Persulphate	Yellow	320	0.025	8
Carbonate	Yellow	305	0.056	9, 10
Tiron	Violet	500	0.031	11
Ceromolybdic heteropoly acid	Yellow	380	0.045	12
Thenoyltrifluoroacetone	Reddish brown	440	0.015	13—15
Molybdocerophosphoric acid	Yellow	318	0.091	16
Triflupromazine hydrochloride	Red	503	0.021	17
N-Phenylbenzohydroxamic acid	Orange	460	0.030	1
N-*p*-chlorophenylcinnamohydroxamic acid (CPCHA)	Orange	460	0.019	—

III. The data given in Table III clearly indicate that the proposed method is highly sensitive and micro amounts of cerium can be determined precisely and accurately. The cerium(IV)-CPCHA complex is highly stable in comparison to the complexes formed with other reagents in most of these methods and hence, there is no time limit for the measurement of absorbance after extraction. Most of these methods suffer from serious interferences caused by many common ions normally associated with cerium. In comparison, the proposed method is quite selective and free from the interference.

An advantage of the newly developed method is that the colour development procedure itself takes care of the conversion of cerium(III) to cerium(IV) by atmospheric oxidation during the 30 minute period of occasional stirring. Finally, the method is simple and free from the regid control of experimental variables.

Determination of Complex Composition

The stoichiometric composition of the cerium(IV-CPCHA complex was determined by the mole ratio method[18]. The result obtained indicates the formation of 1 : 4 (Ce : CPCHA) complex. The composition was further confirmed by the elemental analyses of the dried solid complex. The complex was precipitated by the addition of an ethanolic solution of the reagent to the hot solution of cerium(IV) at pH 8—9. It was filtered, washed and dried at 120 °C. The dried complex was analysed for cerium by igniting a known weight of it to the cerium(IV) oxide. The carbon, hydrogen, nitrogen, and chlorine were estimated by the usual combustion methods. The results of the elemental analyses indicate that its composition is $Ce(C_{15}H_{11}NO_2Cl)_4$ (found Ce, 11.26%; C, 58.72%; H, 3.68%; N, 4.48%; Cl, 11.64% calculated Ce, 11.38%; C, 58.54%; H, 3.60%; N, 4.55%; Cl, 11.52%).

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SAŽETAK

Ekstrakcija i spektrofotometrijsko određivanje cera(IV) s *N*-*p*-klorofenilcinamohidroksamatnom kiselinom

B. S. Chandravanshi i V. K. Gupta

Opisana je nova metoda za ekstrakciju i spektrofotometrijsko određivanje cera(IV), bazirana na osjetljivoj reakciji *N*-*p*-klorofenilcinamohidroksamne kiseline i cera(IV) pri čemu nastaje narandasto obojeni kompleks koji se iz alkalnih otopina kvantitativno ekstrahira u kloroform. Određen je sastav ekstrahiranog kompleksa kao i optimalni uvjeti za određivanje.

Opisana metoda je komparirana s ostalim poznatim metodama za određivanje cera.