

***p*-Chloro Substituted Cinnamohydroxamic Acids as Analytical Reagent for Cerium. Spectrophotometric Determination with *N*-Phenyl-*p*-Chlorocinnamohydroxamic Acid**

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A selective and sensitive method for the solvent extraction and spectrophotometric determination of cerium(IV) with *N*-phenyl-*p*-chlorocinnamohydroxamic acid (*N*-*p*-*p*-Cl-CHA) has been described. It forms a red colored complex with cerium and the complex can be extracted with chloroform at pH 9 to 10. The effect of the pH, reagent concentration, extraction time, stability of color, diverse ions and stoichiometry of the complex is discussed.

INTRODUCTION

Hydroxamic acids are the selective and sensitive reagents for the spectrophotometric determination of various metal ions¹⁻¹⁰. *N*-Phenyl-benzohydroxamic acid (PBHA) and *N*-*p*-chlorophenylbenzohydroxamic acid (*p*-Cl-BHA) have been used for the solvent extraction and spectrophotometric determination of cerium(IV)^{11,12}. Later *N*-*p*-tolylbenzohydroxamic acid (*p*-TBHA), having the molar absorptivity (ϵ) of 4600 dm³ mol⁻¹ cm⁻¹ at 460—470 nm has been reported as a selective and sensitive reagent for cerium¹³. The substituted cinnamohydroxamic acids have elicited special interest. The molar absorptivity of the cerium complex of *N*-phenyl-*p*-chlorocinnamohydroxamic acid (*N*-*p*-*p*-Cl-CHA) is 5500 dm³ mol⁻¹cm⁻¹ compared to *p*-TBHA. Moreover the cinnamohydroxamic acids method can tolerate large amounts of diverse ions in the determination of cerium(IV). The improved sensitivity of the reaction as reflected by a conspicuous increase in molar absorptivity may presumably be attributed to the increased conjugation in the cinnamohydroxamic acid caused by the CH=CH linkage. A number of unsaturated *N*-aryl hydroxamic acids have been synthesized¹⁴ and complexation has been studied for Ce(IV). A detailed study with *N*-phenyl-*p*-chlorocinnamohydroxamic acid has shown that the determination of cerium(IV) is rapid, selective and sensitive.

EXPERIMENTAL

All chemicals used were of A. R. and E. Merck quality. The preparation and properties of the reagents have been described elsewhere¹⁴.

0.2% w/v reagent solutions of *p*-chloro-substituted cinnamohydroxamic acids were prepared in pure ethanol.

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A standard cerium solution was prepared by dissolving the required amount of ceric sulphate and its final concentration (9.9×10^{-4} mol dm⁻³) was determined volumetrically¹⁵.

A VSU2P spectrophotometer was used for the photometric measurement.

2 ml of cerium solution were put into a 60 ml separatory funnel, to which were added 2 ml of 0.2% w/v reagent solution prepared in ethanol and 6 ml of pH 9 buffer solution. To extract the complex 10 ml of chloroform were added. The contents were shaken vigorously for 5–10 min and the phases allowed to separate. The organic phase was dried over anhydrous sodium-sulphate and transferred into a 25 ml volumetric flask. To ensure complete recovery of the cerium, the extraction was repeated with 1 ml of the reagent solution and the anhydrous extract was diluted to 25 ml with chloroform. The absorbance spectra of the coloured extract was measured against the reagent blank.

RESULTS AND DISCUSSION

Cerium *N*-*p*-chloro-substituted cinnamohydroxamic acids complexes give a reddish brown color with a maximum absorption of around 470 nm at pH 9.0. Nitro-substituted cinnamohydroxamic acids could not be used for the extraction of cerium since they decompose at pH 9.0.

Several organic solvents such as chloroform, carbon tetrachloride, benzene, diethyl ether, ethylacetate and iso-amyl alcohol have been studied for extraction purposes. However, chloroform has been found to be the most suitable solvent.

The spectral characteristics of the cerium(IV) complexes of the various *N*-arylhydroxamic acids studied are recorded in Table I. The absorption maxima are generally not sharp, showing a hump at 470 nm. These spectra show a hyperchromic effect with respect to that of PBHA.

TABLE I

*Extraction and Spectrophotometric Determination of Cerium(IV)-
-p-Chloro Substituted Cinnamohydroxamate Complexes*

Cerium $c = 2 \times 9.9 \times 10^{-4}$ mol dm⁻³ (in 25 ml of Chloroform)

Colour of the Complex: Reddish Brown

Wavelength $\lambda = 470$ nm.

Cinnamohydroxamic Acids	pH of extraction	Molar absorptivity (dm ³ mol ⁻¹ cm ⁻¹)
<i>N</i> -phenyl- <i>p</i> -chloro-	8.0	4.1×10^3
	8.6	5.2×10^3
	9.0	5.5×10^3
	9.5	5.5×10^3
	10.0	5.5×10^3
	10.2	3.8×10^2
	10.4	3.3×10^3
<i>N</i> - <i>m</i> -tolyl- <i>p</i> -chloro-	9.0	5.3×10^3
	10.0	5.3×10^3
<i>N</i> - <i>p</i> -tolyl- <i>p</i> -chloro-	9.0	5.3×10^3
	10.0	5.3×10^3
	10.0	5.3×10^3
<i>N</i> - <i>p</i> -chlorophenyl- <i>p</i> -chloro-	9.0	5.3×10^3
	10.0	5.3×10^3

The maximum colour intensity is obtained at pH 9.0–10.0, beyond this the extraction is incomplete.

0.2% chloroform solution of hydroxamic acids have an absorbance of 0.02 at 470 nm; hence, all the measurements were taken against the reagent as blank. The spectral measurements are reproducible (± 0.01 absorbance unit).

Determination of Cerium(IV) with N-p-p-Cl-CHA

The effects of the following variables in the reaction of *N-p-p-Cl-CHA* with Ce(IV) were investigated.

Beer's Law:

The system obeys Beer's law over the range of 0.2—30 ppm of cerium at 470 nm.

Effect of pH:

The effects of the following variables in the reaction of *N-p-p-Cl-CHA* color intensity was obtained at pH 9 to 10.

Effect of Reagent Concentration:

Extraction of cerium was studied with varying amounts of reagent concentration. The results showed that a single extraction with 2 ml of 0.2% w/v reagent solution was enough for the extraction of cerium. The lower concentration of the reagent gave incomplete extraction.

Extraction Time and Stability:

Extraction of the cerium complex is very rapid under the conditions recommended in the analytical procedure. Shaking for 2—3 min was enough to attain equilibrium when the reagent was added to the aqueous phase.

The cerium complex is stable for several days. The absorbance remains unchanged for at least 10 days.

Effect of Diverse Ions:

The recommended procedure was followed to study the interference due to various diverse ions in the direct spectrophotometric determination of cerium(IV) with *N-phenyl-p-chlorocinnamohydroxamic acid*.

Cerium (20 $\mu\text{g}/25$ ml) can be determined in the presence of the following ions:

Ag⁺(100 mg); Be²⁺(100 mg); Mg²⁺(100 mg); Mo⁶⁺(40 mg);
Ca²⁺(100 mg); Sr²⁺(100 mg); Cu²⁺(100 mg); Cd²⁺(100 mg);
Zn²⁺(100 mg); Ni²⁺(100 mg); Pb²⁺(100 mg); Ga³⁺(60 mg);
UO₂²⁺(60 mg); Ta⁺⁵(80 mg); Nb⁺⁵(80 mg); Co²⁺(100 mg);
Ba²⁺(100 mg); Hg²⁺(100 mg); Mn²⁺(100 mg); La³⁺(80 mg);
Sb³⁺(100 mg); As³⁺(80 mg); Fe³⁺(100 mg); In³⁺(80 mg);
Cr³⁺(80 mg); Ti⁴⁺(30 mg); Zr⁴⁺(30 mg); Th⁴⁺(80 mg);
V⁵⁺(30 mg) and rare earths (100 mg).

NO₂⁻(80 mg); F⁻(80 mg); Cl⁻(80 mg); Br⁻(80 mg); I⁻(80 mg); SO₄⁻²(80 mg) and PO₄⁻³(40 mg).

The complexing ions such as citrate and tartrate had no such effect on the extraction and determination of cerium(IV).

Precision and Accuracy:

To test the reliability of the present method, standard cerium samples were analyzed. The results represented in Table II show that cerium can be determined precisely and accurately.

TABLE II

Analytical Data on the Extraction of Cerium(IV) N-Phenyl-p-Chlorocinnamohydroxamic Acid

pH = 9.0

Colour of the Complex: Reddish Brown

Wavelength $\lambda = 470$ nm.

Cerium taken ppm	Absorbance	Cerium found ppm	Standard deviation*
2	0.078	1.98	± 0.02
4	0.158	3.99	± 0.01
6	0.238	6.01	± 0.01
8	0.316	8.01	± 0.01
10	0.395	10.02	± 0.02
20	0.791	20.01	± 0.01
30	1.186	30.00	± 0.01

* Average of eight determinations.

Stoichiometry of the Complex:

Job's continuous variation method¹⁶ and molar ratio method¹⁷ were used to determine the ratio of cerium(IV) to *N*-phenyl-*p*-chlorocinnamohydroxamate in extracted species at pH 9.0. The results indicate that the ratio of cerium to ligand is 1 : 4.

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SAŽETAK

***p*-Klor-supstituirane cinamohidroksamne kiseline kao analitički reagensi za cerij. Spektrofotometrijsko određivanje s pomoću *N*-fenil-*p*-klorcinamohidroksamne kiseline**

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Opisana je osjetljiva i selektivna metoda za ekstrakciju i spektrofotometrijsko određivanje cerija(IV) s pomoću *N*-fenil-*p*-klorcinamohidroksamne kiseline koja s tim ionom gradi crveno obojeni kompleks; taj se može ekstrahirati kloroformom pri $9 < \text{pH} < 10$. Proučen je utjecaj pH, koncentracije reagensa, trajanja ekstrakcije, različitih drugih iona, a također i sastav kompleksa.

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