

APPENDIX II

REPRINTED FROM

# BUNSEKI KAGAKU

## SECTION E

Volume 33

1984

The Japan Society for Analytical Chemistry

26-2, Nishigotanda 1-chome, Shinagawa-ku, Tokyo 141, JAPAN

© 1984

NEW SUBSTITUTED HYDROXAMIC ACIDS FOR SPECTROPHOTOMETRIC  
DETERMINATION OF CERIUM(IV)Y.K.Agrawal<sup>®</sup> and K.T.JohnPharmacy Department, Faculty of Technology & Engineering,  
M.S.University of Baroda, Kalabhavan, Baroda-390001,  
INDIA.

A sensitive and selective method for the solvent extraction and spectrophotometric determination of cerium(IV) with N-p-Chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid has been described. It forms a reddish brown coloured complex with cerium(IV) which can be extracted into chloroform at pH 9-10 and the molar absorptivity is  $8.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at 465 nm. The effects of pH, reagent concentration, extraction time and stability of the complex are discussed.

## INTRODUCTION

Substituted hydroxamic acids have received a great deal of attention as colorimetric and gravimetric reagents for metals<sup>1)-9)</sup>. Among the rare earths, it has been found that cerium(IV) forms stable complexes with N-arylhydroxamic acids which are quantitatively extractable into different organic solvents in pH 8-10 range<sup>10)-12)</sup>. Substituted cinnamohydroxamic acids have elicited special interest in the extraction and spectrophotometric determination of Ce(IV) due to its high sensitivity and selectivity<sup>13)</sup>. On the above basis, a number of substituted N-arylhydroxamic acids were synthesized and complexation has been studied for Ce(IV). A comparison on the selectivity and sensitivity with other reported hydroxamic acids is shown in Table 1. N-p-Chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid has been studied in detail since it proved to be the best reagent for the rapid, sensitive and selective determination of cerium(IV).

## EXPERIMENTAL

All chemicals used were of A.R. and E.Merck quality.

The hydroxamic acids used were synthesised as described elsewhere<sup>19)</sup>. Reagent solutions of the N-arylhydroxamic acids 0.2% (w/v) in ethanol were used for complexation.

The standard buffer solutions in the pH ranges 6.0-7.4 and 10.0-11.6 were prepared with 0.1 M  $\text{KH}_2\text{PO}_4$  + 0.5 M borax and 0.025 M borax + 0.1 M NaOH (also 0.05 M  $\text{NaHCO}_3$  + 0.1 M NaOH) respectively, as described elsewhere<sup>17)</sup>.

A standard solution of cerium(IV) was prepared by dissolving required amount of cerium(IV) ammonium sulphate in redistilled water and its final concentration ( $1.2 \times 10^{-3}$  M) was determined by spectrophotometry<sup>10)</sup> and titrimetry<sup>18)</sup>.

Absorbance measurements were made in C.Z.Jena VSU2-P with 1 cm quartz cells.

### General Procedure

One ml of cerium(IV) solution ( $1.2 \times 10^{-3}$  M) and 3 ml of 0.2% (W/V) reagent solution in ethanol were transferred to a 60-ml separatory funnel. The pH was adjusted to 9.0 with borax buffer<sup>17)</sup> and the volume of the aqueous phase to 25 ml, and the complex was extracted into 10 ml chloroform. The chloroform layer was separated after shaking for 3-5 min, dried over anhydrous sodium sulphate and transferred to a 25-ml volumetric flask. To ensure the complete recovery of cerium, the aqueous layer was treated with 2 ml of reagent solution and extracted with 2 x 5 ml of chloroform. The extracts were diluted to 25 ml with chloroform and the absorbance was measured against the reagent blank.

### RESULTS AND DISCUSSION

Cerium-N-p-Chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid complex gives a reddish brown coloured extract at pH 9-10, having a maximum absorbance at 465 nm with a molar absorptivity  $8.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . The characteristics of the cerium(IV) complexes of the several N-arylhydroxamic acids studied are recorded in Table 2. The enhanced sensitivity of the reagent as reflected by an increased molar absorptivity is due to the increased conjugation and presence of the alkoxy groups in the C-phenyl ring. It is noted that the molar absorptivity of the complex is increased with the introduction of chlorine to the para position of N-phenyl (Table 2) presumably due to the resonance stabilization of the conjugate base anion by the electron withdrawing ability of the chlorine atom. This allows positive charge built upon N and thereby stabilize the anion by induction. Separation of C-phenyl ring from the functional carbonyl group by a tertiary carbon yields a decreased sensitivity in the reagent towards cerium(IV), due to the decreased conjugation in the reagent.

#### Effect of pH

The extraction behaviour of cerium(IV) complex was studied in the pH range<sup>17)</sup> 6-11 (Table 3). The results given in Table 3 show that the extraction commences from pH 7.0 and it is quantitative around pH 8.0. The extraction curve remains almost constant in the pH range 8-11. The extraction at higher pH (> 11) gives the turbidity. The optimum pH range for quantitative extraction is 9-10.

#### Beer's Law

Beer's law is obeyed in the concentration range of 0.3 to 13 ppm of cerium(IV) (in the extract) at 465 nm, and Sandell sensitivity is  $0.016 \mu\text{g cm}^{-2}$ .

#### Effect of reagent concentration

Extractions of cerium were studied with varying concentrations of the reagent. The results showed that a single extraction with 2 ml of 0.2% W/V reagent solution in ethanol (the absorbance of the reagent solution vs  $\text{CHCl}_3$  at 465 nm is 0.001) was enough for the complete recovery of  $167.5 \mu\text{g}$  cerium per 25 ml of solution. Although the excess reagent has no adverse effect on the extraction of cerium, lower concentration of the reagent gave incomplete extraction. The increased amount of the alcohol (> 10%) tends to reduce the extraction percentage.

#### Extraction time and stability

Extraction of 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-p-Chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid.

Cerium (6.7 ppm in the 25 ml extract) can be determined (standard deviation C. 0.03, n=6) in the presence of the following ions:

Ag<sup>+</sup>(100 mg); Be<sup>2+</sup>(100 mg); Mg<sup>2+</sup>(100 mg); Ca<sup>2+</sup>(100 mg); Sr<sup>2+</sup>(100 mg); Cu<sup>2+</sup>(100 mg); Cd<sup>2+</sup>(100 mg); Zn<sup>2+</sup>(100 mg); Ni<sup>2+</sup>(100 mg); Pb<sup>2+</sup>(100 mg); Co<sup>2+</sup>(100 mg); Ba<sup>2+</sup>(100 mg); Hg<sup>2+</sup>(100 mg); Mn<sup>2+</sup>(100 mg); Ga<sup>3+</sup>(60 mg); La<sup>3+</sup>(100 mg); Sc<sup>3+</sup>(80 mg); Sb<sup>3+</sup>(100 mg); As<sup>3+</sup>(80 mg); Fe<sup>3+</sup>(100 mg); In<sup>3+</sup>(80 mg); Cr<sup>3+</sup>(80 mg); Ti<sup>4+</sup>(30 mg); Zr<sup>4+</sup>(30 mg); Th<sup>4+</sup>(80 mg); V<sup>5+</sup>(30 mg); Ta<sup>5+</sup>(80 mg); Nb<sup>5+</sup>(80 mg); Mo<sup>6+</sup>(40 mg); UO<sub>2</sub><sup>2+</sup>(60 mg); and rare earths (Gd, Pr, Nd, Sm, etc.) (100 mg).

NO<sub>2</sub><sup>-</sup>(80 mg); NO<sub>3</sub><sup>-</sup>(80 mg); F<sup>-</sup>(80 mg); Cl<sup>-</sup>(80 mg); Br<sup>-</sup>(80 mg); I<sup>-</sup>(80 mg); SO<sub>4</sub><sup>2-</sup>(80 mg) and PO<sub>4</sub><sup>3-</sup>(40 mg).

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

#### Precision and accuracy

To test the reliability of the present method, standard cerium samples were analysed. The results represented in Table 4 show that cerium can be determined accurately.

The cerium standard and monazite ore samples were obtained from Indian Rare Earths. The sea water samples were collected from Bombay and used (one litre) as such for the determination of cerium<sup>14</sup>. Values for standard cerium analysis were obtained by emission spectrographic and radioactive tracer technique (analysis was carried at Radiochemistry Division, B.A.R.C., Bombay)<sup>20-21</sup>.

The cerium samples were dissolved in 12 M HCl, oxidized with HNO<sub>3</sub> and evaporated to dryness. The residue was redissolved in 1 M H<sub>2</sub>SO<sub>4</sub>. Then 0.1 M potassium permanganate solution was added drop by drop until a pink colour persisted for 5 min. The solution was finally diluted to 100 ml with 0.05 M H<sub>2</sub>SO<sub>4</sub>.

#### Stoichiometry of the complex

Job's continuous variation method<sup>22</sup> and molar ratio method<sup>23</sup> were used to determine the ratio of cerium(IV) to N-p-Chlorophenyl-3,4,5-trimethoxycinnamohydroxamate in the extracted species at pH 9.0 which showed that cerium to ligand ratio is 1 : 4.

Table 1 Comparison of spectrophotometric methods for the determination of cerium

Hydroxamic acid	$\lambda_{\max}$ (nm)	Molar absorptivity $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	Reference
N-Phenylbenzo-	460	3740	10
N-p-Tolylbenzo-	465	4600	14
N-p-Tolyl-p-chlorobenzo-	460	4500	15
N-p-Tolylcrotono-	460	3700	16
N-Phenyl-p-chlorocinnamo-	470	5500	13
N-p-Tolyl-p-chlorocinnamo-	470	5300	13
N-p-Chlorophenyl-p-chlorocinnamo-	470	5300	13
N-p-Chlorophenyl-3,4,5-trimethoxycinnamo-	465	8500	Present work

Table 2 Extraction and spectrophotometric determination of cerium(IV) with N-aryl-hydroxamic acids

Cerium : 6.7 ppm (in the extract) pH : 8-10 Solvent : Chloroform Reagent : 3 ml of 0.2% alcoholic solution.

Compd. No.	Hydroxamic acid	Colour of chloroform extract	Wavelength of maximum absorption (nm)	Molar absorptivity ( $\epsilon$ ) $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	Sandell sensitivity $\mu\text{g cm}^{-2}$
I	N-p-Chlorophenyl-3,4,5-trimethoxycinnamo-	RB	465	$8.5 \times 10^3$	0.016
II	N-Phenyl-2,3-dimethoxycinnamo-	RB	460	$7.5 \times 10^3$	0.018
III	N-p-Chlorophenyl-p-butoxybenzo-	RB	460	$6.5 \times 10^3$	0.021
IV	N-Phenyl-p-butoxybenzo-	RB	460	$5.9 \times 10^3$	0.024
V	N-p-Chlorophenyl-p-chlorophenoxyisobutyro-	YO	440	$4.25 \times 10^3$	0.033
VI	N-Phenyl-p-chlorophenoxyisobutyro-	YO	440	$3.9 \times 10^3$	0.036

RB = Reddish brown YO = Yellowish orange

Table Effect of pH on the extraction of cerium(IV)-N-p-Chlorophenyl-3,4,5-trimethoxycinnamohydrozamic acid complex  
 Cerium = 8.7 ppm (in the extract) Reagent = 3 ml of 0.2% alcoholic solution

pH	Absorbance at 465 nm	% Extraction
6.0	0.073	17
6.3	0.145	35
7.0	0.220	52
7.4	0.350	85
8.0	0.410	100
8.5	0.410	100
9.0	0.410	100
9.5	0.410	100
10.0	0.410	100
11.0	0.410	100
11.6	0.400	97

Table 4 Determination of cerium in standard samples and sea water

Cerium sample	Recommended value <sup>14,21</sup> (ppm)	Cerium found (ppm) (present method)	Standard deviation (n = 7)	Coefficient of variation
Cerium Standard Sample	2.5	2.5	± 0.005	0.002
Monazite Ore	43%	42.8%	± 0.1%	0.008
Seawater, near Bombay				
Thana (Bridge)	0.005	0.004	± 0.001	0.250
Appolo Bunder	0.003	0.004	± 0.001	0.250
Marine lines	0.003	0.003	± 0.001	0.333
Mahim	0.004	0.005	± 0.001	0.200
Belapur	0.003	0.003	± 0.001	0.333

#### REFERENCES

- 1) A.G.Macdonaldson: Ind. Chem., 36, 512 (1960), 37, 30 (1961).
- 2) U.Priyadarshini, S.G.Tandon: Anal. Chem., 33, 435 (1961).
- 3) D.C.Bhura, S.G.Tandon: Anal. Chim. Acta, 53, 379 (1971).
- 4) Y.K.Agrawal: Sep. Sci., 8, 613 (1973).
- 5) Y.K.Agrawal: Anal. Lett., 7, 729 (1974).
- 6) Y.K.Agrawal: Anal. Lett., 5, 863 (1972).
- 7) Y.K.Agrawal: Sep. Sci., 10, 167 (1975).
- 8) Y.K.Agrawal: Sep. Sci., 8, 709 (1973).

- 9) Y.K.Agrawal: Anal. Chem., 47, 940 (1975).
- 10) P.Murugaiyan, M.Shankar Das: Anal. Chim. Acta, 48, 155 (1969).
- 11) S.A.Patel, Y.K.Agrawal: Microchem. J., 25, 48 (1980).
- 12) Y.K.Agrawal: Z. Anal. Chem., 285, 258 (1977).
- 13) R.K.Jain, Y.K.Agrawal: Croat. Chem. Acta, 53, 471 (1980).
- 14) Y.K.Agrawal: Mikrochim. Acta, 2, 595 (1976).
- 15) Y.K.Agrawal, H.L.Kapoor: Ann. di Chim., 66, 117 (1976).
- 16) B.S.Chandravanshi, V.K.Gupta: Indian J. Chem., 16, 548 (1978).
- 17) J.A.Dean (Ed.): "Lange's Handbook of Chemistry", 12th ed., (1979), (McGraw-Hill Book Company).
- 18) J.Bassett, R.C.Denny, G.H.Jeffery, J.Mendham: "Vogel's Textbook of Quantitative Inorganic Analysis", 4th ed., (1979), (ELBS, Longman, London).
- 19) Y.K.Agrawal, S.G.Tandon: J. Chem. Eng. Data, 16, 371 (1971); 16, 495 (1971).
- 20) R.E.Michaelis: Am. Soc. Testing Materials Spec. Tech. Publ. No.58-E, Philadelphia (1963).
- 21) V.P.Guinn and H.R.Lukens, Jr.: in G.H.Morrison, Ed., "Trace Analysis. Physical Methods", (1965), (Interscience Publishers, New York).
- 22) P.Job: Ann. Chim. (Paris), 9, 113 (1928).
- 23) J.H.Yoe and A.L.Jones: Ind. Eng. Chem. Anal. Ed., 16, 111 (1944).

Keyword phrases

Cerium(IV) extraction-spectrometry using new substituted Hydroxamic acids.

(Received May 23, 1983)