

Solvent extraction and spectrophotometric determination of lanthanides with N-phenylcinnamohydroxamic acid

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The solvent extraction and spectrophotometric determination of lanthanides with N-phenylcinnamohydroxamic acid (PCHA) is described. Lanthanum (III), praseodymium(III), neodymium(III), samarium(III), gadolinium(III), and terbium(III) form 1:3 yellow coloured binary complexes (λ_{\max} 380 nm) with PCHA which are extractable quantitatively into chloroform, at pH 9.0. Sensitivity of the spectrophotometric determination is enhanced by the addition of xylenol orange to the organic extract having maximum absorbance between 590 and 610 nm. Efforts have been made to study the extraction equilibria by calculating the extraction constants and the two phase stability constants of the complexes. The possible separation of the lanthanides from each other has been studied by evaluating separation factor(s) and $pH_{1/2}$ (pH of 50% extraction). The lanthanides are determined in standard United State Geological Samples (USGS) and IAEA Soil-5 samples.

The potential of hydroxamic acids as analytical reagents has already been established¹⁻³. Among hydroxamic acids, N-phenylbenzohydroxamic acid (PBHA) is most extensively used in solvent extraction and the gravimetric determination of various metal ions. It has been shown that an increase in conjugation in PBHA by the introduction of side chain double bonds ($-\text{CH}=\text{CH}-$) between the carbon atom of the carbonyl and the phenyl group causes a significant increase in the molar absorptivity of the metal complexes. The increased conjugation also helps to increase the ionization of the ligand at equilibrium and thereby enhances complexation with metal ions and also provides colour to the complexes, enabling direct spectrophotometric determination to be used. Hence, N-phenylcinnamohydroxamic acid (PCHA) is considered to be a highly selective and sensitive reagent compared to PBHA.

The present paper describes the solvent extraction nature and spectrophotometric determination of the lanthanides viz, lanthanum(III), praseodymium(III), neodymium(III), samarium(III), gadolini-

um(III) and terbium(III) with N-phenylcinnamohydroxamic acid (PCHA).

Experimental

All the chemicals used were of AnalaR and GR grades of BDH or E. Merck, respectively unless otherwise specified. N-phenylcinnamohydroxamic acid (PCHA) was synthesised as described elsewhere⁴ and its purity was checked by m.p., elemental analysis, TLC, IR and UV spectra. A 0.1% (w/v) solution of the reagent in chloroform (0.1% w/v) was used for all the extractions. Stock solutions of rare earths perchlorates (~ 0.01 M) were prepared by dissolving 0.3258, 1.021, 0.3365, 0.3487, 0.3625 and 0.7477 gr of spec pure oxides of La, Pr, Nd, Sm, Gd and Tb, respectively in minimum quantity of 0.1 N perchloric acid and the metal content was determined by EDTA⁵. Solutions of xylenol orange (0.05% w/v) were prepared in methanol. Triethanolamine buffer, pH range 7-10, was prepared from 0.5 M triethanolamine solution and HCl or HNO₃ (ref. 6).

Spectrophotometric measurements were carried out with Shimadzu UV-VIS 240 recording spectrophotometer. A Systronics (Ahmedabad, India), pH meter model 335, equipped with glass and calomel electrodes, was used for pH measurements.

Extraction of binary complexes

An aliquot of lanthanum (3.85×10^{-5} M) {praseodymium (3.1×10^{-5} M), neodymium (2.62×10^{-5} M) samarium (2.46×10^{-5} M), gadolinium (2.78×10^{-5} M) or terbium (2.76×10^{-5} M)} was transferred into a 60 ml separatory funnel and the pH was adjusted with triethanolamine buffer solution (5 ml). The aqueous phase was equilibrated for 10-15 min with 10 ml of 0.1% solution of N-phenylcinnamohydroxamic acid in chloroform (10 ml, 0.1%) by shaking in a wrist-action shaker at a constant speed. The organic phase was separated, dried over anhydrous sodium sulphate and transferred to a 25 ml volumetric flask. The extraction was repeated with 3 ml of the reagent solution to ensure the complete recovery of the rare earth. The volume was made up to the mark with chloroform and the absorbance was measured at 380 nm against a reagent blank.

Back extraction

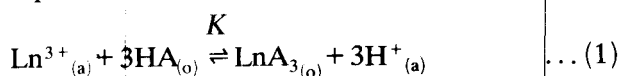
The organic phase was back extracted with 5 ml

of 0.5 M HCl and the rare earth content was determined spectrophotometrically using arsenazo I⁶.

Determination of the ternary complexes

The organic extract, separated and dried after equilibration with the aqueous phase, as described above, was transferred to a 25 ml volumetric flask and 2.0-2.5 ml of 0.05% xylenol orange in methanol was added followed by 7.5 to 8 ml of methanol, so as to keep the chloroform to methanol ratio 3:2. The volume was made upto the mark with chloroform and the absorbance was measured in the range of 590-610 nm against respective reagent blanks.

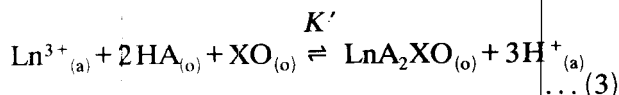
The reaction between the lanthanides (Ln) and N-phenylcinnamohydroxamic acid (HA) can be represented as:



from which

$$\log K = \log D - 3pH - 3\log[\text{HA}]_{(o)} \quad \dots (2)$$

On the addition of xylenol orange (XO) to the organic extract, greenish violet (Ln-HA-XO) ternary complexes are formed by the replacement of one mole of HA with one mole of xylenol orange, as shown by the stoichiometric studies. The formation of these ternary complexes can be represented as:



from which

$$\log K' = \log D - 3pH - 2\log[\text{HA}]_{(o)} + \log[\text{XO}]_{(o)} \quad \dots (4)$$

can be derived.

The distribution constant, *P*, of PCHA was determined by shaking mechanically for 10 min. a series of solutions of the reagent (10 ml, 0.1% in chloroform) with the same volume of aqueous solution of

pH 9.0, adjusted with triethanolamine buffer. After phase separation the absorbance of the organic phase was measured at 292 nm against the solvent. The distribution constant, *P* was calculated from the distribution ratio (*D'*), using the equation,

$$P = D'(1 + K_a/[H^+]) \quad \dots (5)$$

where *K_a* is the acid dissociation constant of the reagent. The log *K*, log(*β*₃·*P'*) and log *K'* values calculated are given in Table 1. The acid dissociation constant (*pK_a*) of PCHA is obtained as 8.46.

Results and discussion

Table 2 summarises the Beer's law range and the molar absorptivity of the binary and ternary complexes. Variation in percentage extraction (% E) for the extraction of La(III), Nd(III), Sm(III), Gd(III) and Tb(III) ions was investigated as a function of pH in the range of 6.0-10.5. The pH range of quantitative extraction of the individual metal ions are shown in Fig. 1. Since the extraction is quantitative at pH 9.0 for all the metal ions studied, the same pH has been selected for further studies to optimise all the parameters.

Slope ratio method⁷ has been adopted for the stoichiometric studies of the binary and ternary complexes. In the case of Ln-PCHA system, the plots of log *D* versus log [PCHA] for all the metal

Table 2—Separation factor, *pH*_{1/2}, extraction constant and stability constants of the lanthanides

Metal	<i>pH</i> _{1/2}	Separation factor(s)	log <i>K</i>	log <i>K'</i>	log(<i>β</i> ₃ · <i>P'</i>)
La	7.35	—	-18.30	-16.54	11.89
Pr	7.05	1.60	-18.10	-16.34	12.09
Nd	6.40	1.22	-18.05	-16.29	12.14
Sm	6.20	1.15	-17.99	-16.23	12.20
Gd	6.35	1.02	-17.98	-16.22	12.21
Tb	5.90	0.89	-18.03	-16.27	12.16

Table 1—Spectral characteristics of binary and ternary complexes

[La(III)] = 3.85 × 10⁻⁵ M; [Pr(III)] = 3.10 × 10⁻⁵ M; [Nd(III)] = 2.62 × 10⁻⁵ M; [Sm(III)] = 2.46 × 10⁻⁵ M; [Gd(III)] = 2.78 × 10⁻⁵ M; [Tb(III)] = 2.76 × 10⁻⁵ M; pH of extraction = 9.0; [PCHA] = 10 ml (0.1% in chloroform), Equilibration time = 10 min

Metal complex	Beer's Law range (μg/ml)	10 ⁻⁴ × (Molar absorptivity) (dm ³ mol ⁻¹ cm ⁻¹)	Beer's Law range (μg/ml)	10 ⁻⁴ × (Molar absorptivity) (dm ³ mol ⁻¹ cm ⁻¹)
La(PCHA) ₃	0.60-23.4	1.18	0.10-3.9	7.0
Pr(PCHA) ₃	0.55-21.9	1.30	0.09-3.8	7.4
Nd(PCHA) ₃	0.52-20.6	1.40	0.08-3.3	8.6
Sm(PCHA) ₃	0.50-19.3	1.55	0.08-3.3	9.2
Gd(PCHA) ₃	0.55-21.8	1.44	0.11 × 4.3	7.2
Tb(PCHA) ₃	0.52-20.6	1.54	0.11 × 4.5	7.0

Values of column IV and V are for "corresponding ML₃ × 0" complexes; Chloroform:methanol::3:2; λ_{max} = 590-610 nm.

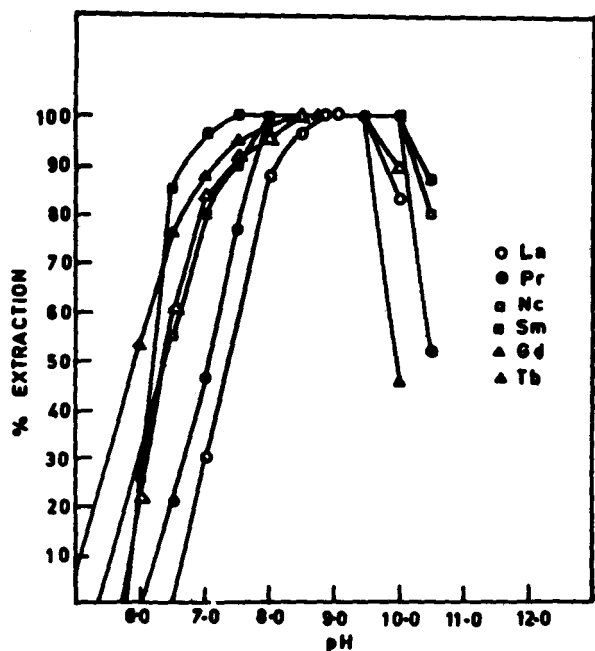


Fig. 1—Extraction of La(III), Pr(III), Nd(III), Sm(III), Gd(III) and Tb(III) as a function of pH

ions at pH 9.0, show slopes of 3 (Fig. 2) which suggests that the stoichiometry of the binary species is 1:3 (metal:ligand).

Similarly in the case of 1N - PCHA - XO system, the plots of log D versus log [xylenol orange] for all the metal ions, at pH 9.0 have slope values close to 1 (Fig. 2), indicating the formation of 1:2:1 (metal: PCHA:xylenol orange) ternary complexes, possible by the replacement of one mole of PCHA by one mole of xylenol orange.

Mutual separation of the lanthanides by the proposed method has been studied by evaluating separation factor (*s*) and pH of 50% extraction of the individual metal ions. The separation factor has been calculated from the distribution ratio of the binary species obtained by the back extraction procedure at pH 9.0. Table 1 also summarizes the values of *s* and pH_{1/2} which enable to formulate the possible separation of the adjacent lanthanides by the present method.

Selectivity of the reagent for lanthanides has been studied by the proposed method extracting the lanthanides in the presence of different ions. The results show that most of the ions studied are not in-

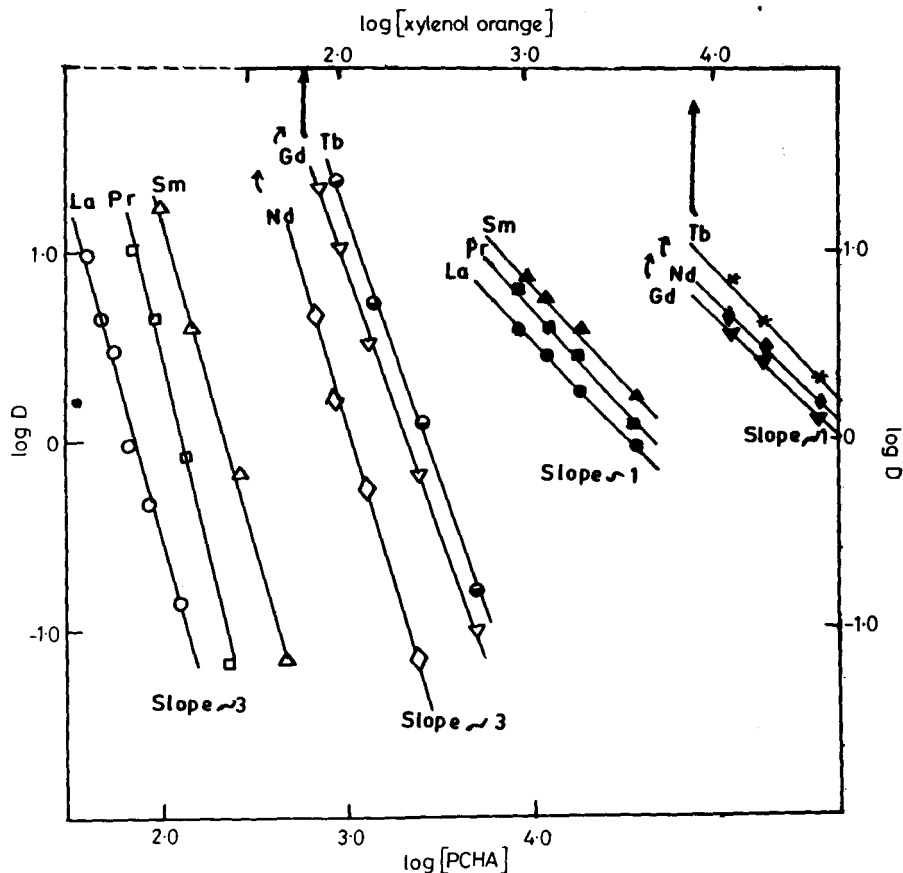


Fig. 2—Variation of log D as a function of log (PCHA) (slope ~ 3) and log (xylenol orange) (slope ~ 1)

Table 3—Determination of rare earths in standard samples
(Samples were from the United States Geological Survey and IAEA Soil-5)

Sample	Rare Earths mg kg ⁻¹									
	Lanthanum		Paraseodymium ^a	Neodymium		Samarium		Gadolinium ^a	Terbium	
	cer. value	found	found	cer. value	found	cer. value	found	found	cer. value	found
BCR-1(52/19)	26.0	25.8	20.5	29.0	29.2	6.6	6.68	4.5	1.0	1.03
ACV-1(74/19)	35.0	35.2	33.0	39.0	38.9	5.9	5.91	5.6	0.70	0.68
GSP-1(17/22)	190.0	189.8	160.0	188.0	188.1	27.1	27.25	18.0	1.30	1.26
G2(108/15)	96.0	96.1	70.5	60.0	59.7	60.0	60.05	45.3	0.50	0.52
W-1	9.8	9.8	6.8	15.0	15.2	3.6	3.58	3.4	0.65	0.66
Soil-5	28.1	27.9	26.3	30.0	29.8	5.42	5.45	4.3	4.67	4.60

Values are average of eight determinators. 'a' the certified values for Pr and Gd have not been reported. cer = certified value

terfering in the extraction. Scandium, being extracted at a considerably lower pH with hydroxamic acids, is not interfering in the lanthanide extraction. However, the interference of yttrium upto 10 mg can be tolerated by masking with sodium fluoride.

The reliability of the method was tested by analysing the standard rare earths, United State Geological Survey (USGS) and IAEA Soil-5, samples. The samples were dissolved in a mixture of perchloric acid and nitric acid and evaporated to dryness. The residue was re-dissolved in 1M HClO₄ and diluted to 250 ml with distilled water. An aliquot of the solution was taken for the extraction and determination of rare earth. The data obtained are given in Table 3.

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References

- 1 Agrawal Y K, *Rev Anal Chem*, 5 (1980) 3.
- 2 Patel S A & Agrawal Y K, *Rev Anal Chem*, 4 (1980) 232.
- 3 Majumdar AK, *N-benzoylphenylhydroxamine and its analogues* (Pergamon, London) (1971).
- 4 Tandon S G & Bhattacharya S C, *J chem eng Data*, 7 (1962) 553.
- 5 Kolthoff I M & Elving P J, *Treatise on analytical chemistry Part-II, Analytical chemistry of the elements*, Vol. 8 (1953) 56.
- 6 Marzenko Z, *Spectrophotometric determination of elements*, (Ellis Horwood, Chichester) (1976).
- 7 Yoe & J H & Harvey A E, *J Am chem Soc*, 17 (1960) 648.