

Separation & Gravimetric Determination of Ce(III), La(III), Pr(III), Nd(III), Sm(III) & Gd(III) Using *N-p*-Chlorophenyl-*m*-nitrobenzohydroxamic Acid

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N-p-Chlorophenyl-*m*-nitrobenzohydroxamic acid is used as a precipitating reagent for the gravimetric determination of Ce³⁺, La³⁺, Pr³⁺, Nd³⁺, Sm³⁺ and Gd³⁺. The optimum conditions of precipitation of these rare earths indicate that by proper control of pH and judicious use of masking agents they could be separated and determined gravimetrically from several metal ions.

THE physico-chemical properties¹ of *N-p*-chlorophenyl-*m*-nitrobenzohydroxamic acid² (CPNBHA) reveal that it is a good complexing reagent and reacts with several rare earths to form solid complexes which can be weighed directly after drying at 110°. In the present note the use of CPNBHA as a reagent for gravimetric determination of Ce³⁺, La³⁺, Pr³⁺, Nd³⁺ and Gd³⁺ and their separation from common metal ions are described.

All the chemicals used were of GR and Analar grades of E. Merck and BDH respectively unless otherwise stated.

The stock solutions of respective rare earths were prepared by dissolving weighed quantities of their nitrates and their final concentrations determined volumetrically³.

1% solutions of masking agents potassium cyanide, oxalate, citrate and Mg-EDTA were prepared by dissolving the requisite amounts in double distilled water in each case separately⁴.

Procedure for gravimetric determinations—A solution (10 ml) of rare earth and about 500 ml distilled water were heated on a water-bath at 60°. Reagent solution (20 ml, 0.01M) in dioxane was added dropwise with constant stirring followed by 0.01M ammonium hydroxide until complete precipitation occurred. The pH of precipitations for rare earths are given in Table 1. The granular complex thus obtained was digested for 20-30 min on a water-bath and centrifuged. The precipitate was washed thoroughly with hot water and finally with 20% aq. dioxane (10×10 ml). It was filtered through a fine porosity filter paper and mounted on a steel planchette. The complexes were dried and weighed as (C₁₃H₈N₂O₄Cl)₂M. All the complexes gave satisfactory elemental analysis.

Separation of La, Ce, Pr, Nd, Sm and Gd from common metal ions: (i) *Using masking agents*—Into 10 ml rare earth solutions (0.001M) known amounts of desired foreign metal ions were added and diluted to 500 ml. The pH was adjusted. Then 10 ml of 1% KCN solution was added and the contents were heated to 60°. The reagent solution

TABLE 1 — GRAVIMETRIC DETERMINATIONS OF RARE EARTHS WITH *N-p*-CHLOROPHENYL-*m*-NITROBENZOHYDROXAMIC ACID

Taken (mg)	Wt of ppt (mg)	Found (mg)	Taken (mg)	Wt of ppt (mg)	Found (mg)
La ³⁺ ; pH 6.2-7.0			Pr ³⁺ ; pH 8.5-9.0		
1.39	10.13	1.39	1.41	10.09	141.40
2.09	15.25	2.09	2.12	15.14	2.10
4.17	30.44	4.19	4.23	30.65	4.25
6.95	50.80	6.96	7.05	50.83	7.05
13.90	101.38	13.89	14.10	101.65	14.10
Ce ³⁺ ; pH 7.2-8.0			Nd ³⁺ ; pH 8.7-9.3		
1.40	10.07	1.39	1.44	10.17	1.40
2.80	20.21	2.79	2.88	19.64	2.78
4.20	30.43	4.20	4.32	30.38	4.30
7.00	50.71	7.00	7.20	50.94	7.21
14.00	101.50	14.01	14.40	101.88	14.42
Sm ³⁺ ; pH 9.5-10.0			Gd ³⁺ ; pH 10.5-10.8		
1.50	10.16	1.49	1.57	10.17	1.55
3.00	20.60	3.02	3.14	20.68	3.15
7.50	51.15	7.50	7.85	51.53	7.85
15.00	102.44	15.02	15.70	103.06	15.70

was added dropwise with constant stirring. The complex thus formed was allowed to stand for about 30 min on a water-bath. It was filtered, washed, dried and weighed as before. The rare earths could be separated from and determined in the presence of Ag⁺, Mn²⁺, Zn²⁺, Cd²⁺, Hg²⁺, Cu²⁺ and Ga³⁺. Rare earths could be precipitated with the reagent and separated from Pb²⁺, Pd²⁺, Be²⁺, Sb³⁺, Sm³⁺, Bi³⁺, Zr⁴⁺ and Ti⁴⁺ with 10 ml 1% citrate and oxalate instead cyanide solution. Rare earths could also be separated from Al³⁺, V⁵⁺ and Mo⁶⁺ by using Mg-EDTA as a masking agent.

(ii) *By adjusting the pH*—10 ml solution of rare earths (0.001M) were diluted to 500 ml and mixed with foreign metal ions. Ag⁺, Cu²⁺, Pb²⁺, Zn²⁺, Cd²⁺, Al³⁺, Th⁴⁺, U⁶⁺ were precipitated below the pH 6.0 with *N-p*-chlorophenyl-*m*-nitrobenzohydroxamic acid using in excess. The precipitate was filtered, washed thoroughly and from mother liquor rare earths were reprecipitated by adjusting the respective pH.

Separation from rare earths—Ce, La, Sm and Gd could be separated from each other by adjusting the pH suitably. The separation of Pr and Nd is difficult since both give precipitate in the same pH range. However, 90-95% separation could be obtained by carefully adjusting the pH at 8.5 and precipitating Pr first then slowly raising the pH up to 9.3 to precipitate Nd. These precipitates were further fractionally crystallized using dioxane as Pr is more soluble than Nd in dioxane.

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