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Ion Chromatography of Lanthanide Metals

INTRODUCTION

In aqueous solution, lanthanide metals are present as trivalent cations. Because the ionic properties are similar, they cannot be separated easily by cation exchange as trivalent cations. However, the selectivity of the ions can be increased with the use of appropriate chelating agents such as α -hydroxyisobutyric acid (HIBA).

Lanthanide metals form complexes with HIBA that lower the affinity of the lanthanide for the cation exchange resin. Two equilibria must be considered—the equilibrium between the eluent and the resin, and the equilibrium between the lanthanide and the lanthanide-HIBA complexes. The difference in stability constants for the lanthanide-HIBA complex implies that each lanthanide will spend more or less time in the eluent depending on

its relative stability with HIBA. This secondary equilibrium permits the separation of the lanthanides because each lanthanide has a different relative stability with HIBA. Therefore, lanthanides that form the most stable complex with HIBA, such as lutetium, will spend relatively more time in the eluent and elute first (see Fig. 1). Lanthanides such as lanthanum, which forms a weaker complex with HIBA, spend relatively less time in the eluent. These metals spend more time in the resin and elute later.

The use of stronger complexing agents, such as oxalate, results in the formation of anionic lanthanide metals. Under these conditions, the lanthanide series may be separated by anion exchange. Because the strongest complexes are the most negatively charged, the elution order is reversed from that of the cation exchange separations (see Fig. 2).

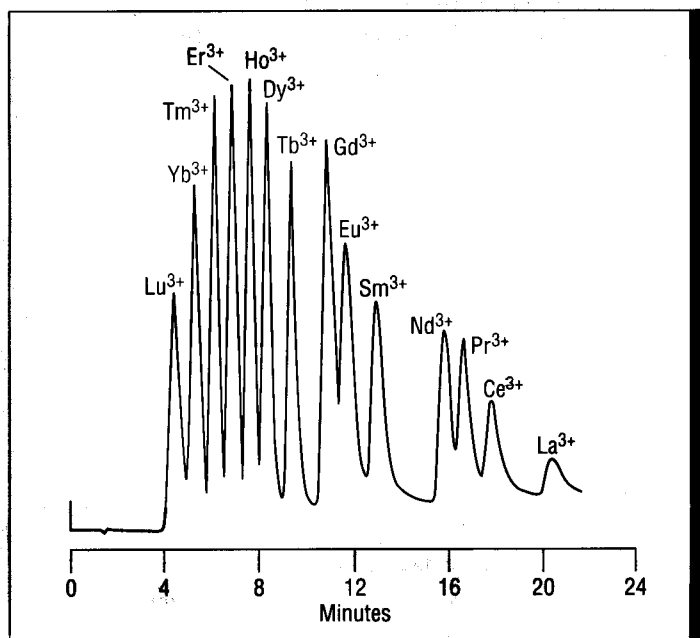


Figure 1 Separation of lanthanide metals by cation exchange (10 ppm each, 0.5 AUFS)

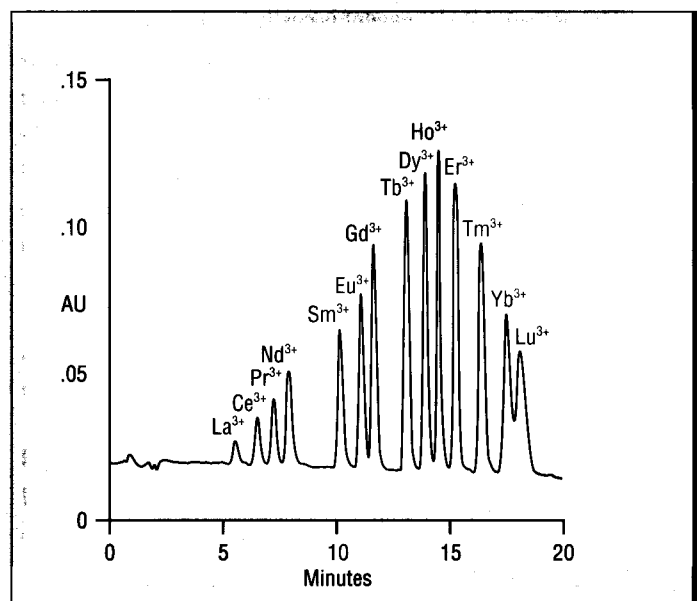


Figure 2 Separation of lanthanides by anion exchange (5.0 ppm each, 0.2 AUFS)

In this technical note, methods are presented for the separation of lanthanides by both cation and anion exchange. Depending on the ratios of the lanthanide elements in a particular sample, either method may be preferred. An anion exchange method for separating transition metals from lanthanides is also presented.

Photometric detection at 530 nm is achieved after postcolumn reaction with the metal complexing reagent 4-(2-pyridylazo)resorcinol (PAR). The detection limits for the metals range from 20 to 40 ppb with a 50- μ L loop.

STANDARDS

1000-mg/L lanthanide metal standards are available from chemical supply companies for use with atomic absorption spectrometry. These standards are always dissolved in dilute acid solutions and can also be used as ion chromatography standards.

CATION EXCHANGE SEPARATION OF LANTHANIDE METALS

Analytes

La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

Discussion of Method

The analytical column used for this method is the IonPac[®] CS3. The separation is achieved using an 18-minute linear gradient of 56 mM to 280 mM α -hydroxyisobutyric acid (HIBA). The total run time is about 23 minutes.

The lanthanide metals are detected by measuring the absorbance at 530 nm of the complex formed with the postcolumn PAR reagent. The prepared PAR reagent is easily oxidized and should be stored under nitrogen or helium.

Recommended Equipment

Dionex Ion or Liquid Chromatograph equipped with a GPM-2 or AGP gradient pump, VDM-2 Detector, and RDM reagent delivery module.

Solutions and Reagents

4-(2-pyridylazo)resorcinol (PAR), (P/N 39672)

α -hydroxyisobutyric acid (HIBA)

Ammonium hydroxide, trace metal grade

Glacial acetic acid, trace metal grade

Lithium hydroxide, monohydrate

Eluent 1: Deionized water

Eluent 2: 0.4 M HIBA

Prepare by dissolving 41.6 g/L of α -hydroxyisobutyric acid in 800 mL of 18-M Ω deionized water. Add 11.3 g lithium hydroxide monohydrate, and stir. The pH should be 4.3.

Post-Reagent: 0.2 mM PAR, 3 M ammonium hydroxide, and 1 M acetic acid

Add 200 mL of 30% ammonium hydroxide to about 400 mL of 18-M Ω deionized water in a 1-L container. Add and dissolve 0.05 g of PAR. Add 57 mL of glacial acetic acid, mix, and dilute to 1 L.

Conditions

Sample Loop Volume: 50 μ L

Columns: IonPac CG3 Guard and CS3 Analytical

Eluents: 1) 18-M Ω Deionized water
2) 0.4 M HIBA

Eluent Flow Rate: 1.0 mL/min

Reagent Flow Rate: 0.7 mL/min

Mixing Device: Membrane Reactor (P/N 35354) and Reaction Coil (P/N 39349)

Detector Wavelength: 530 nm

Gradient Program:	Time	E1	E2
	0.0	86%	14%
	18.0	30%	70%

Reset the gradient pump to time zero conditions after the analysis has been completed. Hold at initial conditions for 10 minutes before the next injection is made.

ANION EXCHANGE SEPARATION OF LANTHANIDE METALS

Analytes

La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

Discussion of Method

The separator column used for this method is the IonPac CS5. The separation is achieved using opposing linear gradients of oxalic acid and diglycolic acid. The gradient is 8 minutes long and the total run time is about 20 minutes. Under these conditions lutetium is not completely resolved from ytterbium.

The lanthanide metals are detected by measuring the absorbance at 530 nm of the complex formed with the postcolumn PAR reagent. Using this method, transition metals will coelute with the

lanthanides. If transition metals are present, refer to the last method presented in this application note, "Simultaneous Determination of Transition Metals and Lanthanide Metals".

Recommended Equipment

Dionex Ion or Liquid Chromatograph equipped with a GPM-2 or AGP gradient pump, VDM-2 Detector, and RDM reagent delivery module.

Solutions and Reagents

4-(2-pyridylazo)resorcinol (PAR), (P/N 39672)

Ammonium hydroxide, trace metal grade

Glacial acetic acid, trace metal grade

Oxalic acid, dihydrate

Lithium hydroxide, monohydrate

Diglycolic acid

Eluent 1: 18-M Ω Deionized water

Eluent 2: 100 mM Oxalic acid and 190 mM lithium hydroxide, monohydrate

Prepare by dissolving 12.61 g oxalic acid dihydrate and 7.97 g lithium hydroxide monohydrate in 1 L of 18-M Ω deionized water. The pH should be 4.8.

Eluent 3: 100 mM Diglycolic acid and 190 mM lithium hydroxide monohydrate

Prepare by dissolving 13.41 g diglycolic acid and 7.97 g lithium hydroxide monohydrate in 1 L of 18-M Ω deionized water. The pH should be 4.8.

Postcolumn Reagent: 0.2 mM PAR, 3 M ammonium hydroxide, 1 M acetic acid

Add 200 mL of 30% ammonium hydroxide to about 400 mL of 18-M Ω deionized water in a 1-L container. Dissolve 0.05 g of PAR in the ammonium hydroxide solution. Add 57 mL glacial acetic acid, mix, and dilute to 1 L.

Conditions

Sample Loop Volume: 50 μ L

Columns: IonPac CG5 Guard and CS5 Analytical

Eluents: 1) 18-M Ω Deionized water
2) 100 mM Oxalic acid
3) 100 mM Diglycolic acid

Eluent Flow Rate: 1.0 mL/min

Reagent Flow Rate: 0.7 mL/min

Mixing Device: Membrane Reactor (P/N 35354) and Reaction Coil (P/N 39349)

Detector Wavelength: 530 nm

Gradient Program:	Time	E1	E2	E3
	0.0	20%	75%	5%
	10.0	50%	25%	25%

Reset the gradient pump to time zero conditions after the analysis has been completed. Hold at initial conditions for 10 minutes before the next injection is made.

SIMULTANEOUS SEPARATION OF TRANSITION METALS AND LANTHANIDE METALS

Analytes

Fe(III), Cu, Ni, Zn, Co, Mn, Fe(II), La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

Discussion of Method

The lanthanide metals can be separated by cation or anion exchange; however, a number of transition metals coelute with lanthanides under the experimental conditions listed in the previous applications. A class separation of lanthanide metals from transition metals is achieved by taking advantage of the electroselectivity differences between transition metal complexes and lanthanide metal complexes. Transition metals form stable monovalent or divalent anionic complexes with pyridine-2,6-dicarboxylic acid (PDCA), while lanthanide elements form stable trivalent anionic complexes with PDCA.

By using PDCA as an eluent chelator, the resulting ionic charge differences between the lanthanide and transition metals permits separation of the transition metals, while the lanthanides are retained at the top of the column. After the transition metals are separated and completely eluted from the analytical column, the lanthanide metals are separated and eluted using the oxalate and diglycolate eluent. The total run time for all the metals is approximately 40 minutes.

The lanthanide metals are detected by measuring the absorbance at 530 nm of the complex formed with the postcolumn PAR reagent.

Recommended Equipment

Dionex Ion or Liquid Chromatograph equipped with a GPM-2 or AGP gradient pump, VDM-2 Detector, and RDM reagent delivery module.

Solutions and Reagents

4-(2-pyridylazo)resorcinol (PAR),
(P/N 39672)

Ammonium hydroxide, trace metal grade

Glacial acetic acid, trace metal grade

Oxalic acid, dihydrate

Lithium hydroxide, monohydrate

Diglycolic acid

Pyridine-2,6-dicarboxylic acid (PDCA),
(P/N 39671)

Sodium hydroxide, 50% solution

Eluent 1: 18-M Ω Deionized water

Eluent 2: 6 mM PDCA, 40 mM sodium hydroxide, and 90 mM glacial acetic acid

Prepare by adding 2.06 mL (3.17 g) sodium hydroxide to 500 mL 18-M Ω deionized water.

Dissolve 1.0 g PCDA, then add 5.15 mL (5.42 g) glacial acetic acid, and dilute to a final volume of 1 L. The pH should be 4.8.

Eluent 3: 100 mM Oxalic acid and 190 mM lithium hydroxide monohydrate

Prepare by dissolving 12.61 g oxalic acid dihydrate and 7.97 g lithium hydroxide monohydrate in 18-M Ω deionized water.

Eluent 4: 100 mM Diglycolic acid and 190 mM lithium hydroxide monohydrate

Prepare by dissolving 13.41 g diglycolic acid and 7.97 g lithium hydroxide monohydrate in 18-M Ω deionized water.

Postcolumn Reagent: 0.2 mM PAR, 3 M ammonium hydroxide, and 1 M glacial acetic acid

Add 200 mL of 30% ammonium hydroxide to about 400 mL of 18-M Ω deionized water in a 1-L container. Dissolve 0.05 g of PAR in the ammonium hydroxide solution. Add 57 mL glacial acetic acid, mix, and dilute to 1 L.

Conditions

Sample Loop Volume: 50 μ L

Columns: IonPac CG5 Guard and
CS5 Analytical

Eluents: 1) 18-M Ω Deionized water

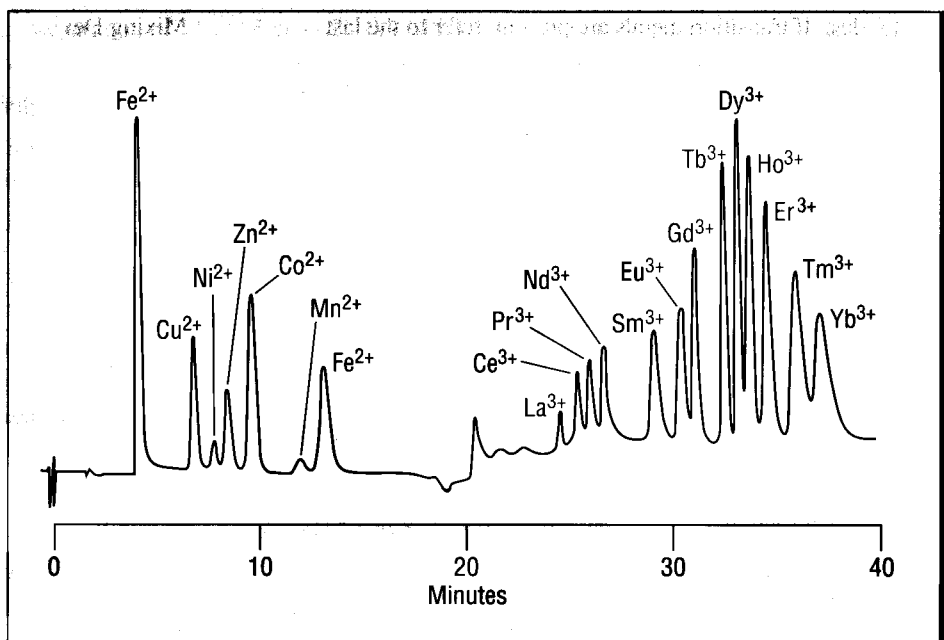


Figure 3 Separation of lanthanides and transition metals in a single injection by ion chromatography

Eluents cont'd.

2) 6 mM PDCA, 40 mM sodium hydroxide, and 90 mM glacial acetic acid

3) 100 mM Oxalic acid and 190 mM lithium hydroxide monohydrate

4) 100 mM Diglycolic acid and 190 mM lithium hydroxide monohydrate

Eluent Flow Rate: 1.0 mL/min

Reagent Flow Rate: 0.7 mL/min

Mixing Device: Membrane Reactor (P/N 35354) and
Reaction Coil (P/N 39349)

Detector Wavelength: 530 nm

Gradient Pump Program:

Time	E1	E2	E3	E4
0.0	0	100	0	0
12.0	0	100	0	0
12.1	100	0	0	0
17.0	100	0	0	0
17.1	40	0	60	0
21.0	40	0	60	0
21.1	20	0	80	0
30.0	51	0	26	23

Reset the gradient pump to initial conditions after the analysis has been completed. Hold at initial conditions before making the next injection.