



New reversed phase-high performance liquid chromatographic method for selective separation of yttrium from all rare earth elements employing nitrilotriacetate complexes in anion exchange mode



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ABSTRACT

Separation of Y from other rare earth elements (REE) is difficult because of similarity of its ionic radius to ionic radii of Tb, Dy and Ho. In the new RP-HPLC system with C₁₈ column, tetra-*n*-butyl ammonium hydroxide (TBAOH) as an ion interaction reagent (IIR), nitrilotriacetic acid (NTA) as a complexing agent at pH = 2.8–3.5, and post column derivatization with Arsenazo III, yttrium is eluted in the region of light REE, between Nd and Sm and is base line separated from Nd and Sm and even from promethium. Simple model employing literature data on complex formation of REE with NTA and based on anion exchange mechanism was developed to foresee the order of elution of individual REE. The model correctly predicted that lanthanides up to Tb will be eluted in the order of increasing Atomic Number (At.No.) but all heavier REE will show smaller retention factors than Tb. Concurrent UV/VIS detection at 658 nm and the use of radioactive tracers together with γ -ray spectrometric measurements made possible to establish a unique elution order of elution of REE: La, Ce, Pr, Nd, Pm, Y, Sm, Er, Ho, Tm, Yb, Eu, Lu, Dy + Gd, Tb, Sc. The real place of Y however, in this elution series differs from that predicted by the model (Y between Sm and Eu). The method described in this work enables selective separation of Y from La, Ce, Pr, Nd, Pm, Sm and all heavier REE treated as a group.

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1. Introduction

Rare earth elements (REE) i.e. scandium, yttrium, lanthanum and lanthanides are used in many areas of modern technology and their role is constantly growing. Except of traditional uses in ceramic and glass industry and as catalysts in petroleum refining, REE find use in production of permanent magnets, phosphors for TV, electronics, rechargeable batteries, night-vision goggles, precision-guided weapons and other defense technology [1–3].

Yttrium in particular is a component of phosphors used in cathode ray tube display of the fluorescent lamps (54% of total consumption of Y₂O₃), as compared to 34% used for ceramic glazes for color control [2]. But yttrium finds also use on the electrodes of some high-performance spark plugs, in the development of superconducting materials and in production of jewelry [4]. A suggestion was made to replace toxic lead in the automobile primer with

yttrium [5]. The demand for REE is steadily increasing and the price usually may strongly depend on the specimen purity. In nature yttrium occurs jointly with other REE. Because of its ionic radius ($r = 90.0$ pm) very similar to those of Er ($r = 89.0$ pm), Ho ($r = 90.1$ pm) and Dy ($r = 91.2$ pm) [6], and the same valency state, Y is usually found together with heavy lanthanides and its separation from all other REE belongs to most difficult tasks of inorganic separations [7]. Therefore every improvement in the methods of separation of REE and in particular separation of Y from the lanthanides should be of interest to specialists in REE separation technology, but also to analytical chemists and radiochemists.

Ion exchange separations of REE were mostly based on elution from strongly acidic sulfonic cation exchangers with buffered solutions of α -hydroxy carboxylic acids like: citric, lactic, mandelic, and α -hydroxyisobutyric acid (HIBA) in which the elution order was from Lu to La [8–13]. This elution order is in agreement with the increasing ionic radius of the REE cations and decreasing complex formation strength of the ligands. The common drawback of these methods was the coelution of Y with Dy and rarer with Ho. It was shown by Dybczyński and Kulisa [11,12] that fairly good separation of Y-Dy pair (with Dy eluting after Y) could be achieved by elution

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with HIBA at 75 °C. The same authors demonstrated reasonable separation of Ho-Dy-Y-Tb group by elution of REE with 68 mM citric acid (pH = 3.18) at 60 °C. In this system Y was eluted after Dy and ahead of Tb [13].

Similar problems with coelution of Y-Dy pair were encountered by the workers employing RP-HPLC columns dynamically modified with *n*-octane sulfonate present in the mobile phase as ion interaction reagent (IIR) and hydroxyacids as eluents [14–17].

Some workers were looking for the new ion exchange systems in which elution position of Y within lanthanide series would be different from that “normally” expected on the basis of its ionic radius. Strelow and Victor [18] observed that Y eluted between Sm and Nd when REE were eluted from Dowex 50W-X4[H⁺] column with hydroxyethylenediaminetetraacetate (HEDTA) at pH = 2.85. Nesterenko and Jones [19] separated REE by high performance chelation ion chromatography on iminodiacetic acid bonded to silica. In this system (elution sequence from La to Lu), Y eluted between Nd and Sm, Gd-Eu and Dy-Ho pairs coeluted. Effective separation of Y from heavy lanthanides on C₁₈ column using *n*-octane sulfonate as IIR and acetic acid as eluent was recently published [20]. However, actual elution positions of the lanthanides lighter than Tb in these conditions were not reported. RP-HPLC with C₁₈ column, 1-octanesulfonate as IIR and nitrilotriacetic acid (NTA) as eluent was used by Kuroda et al. [21] for REE separation with Y eluting immediately after Sm, well separated from Nd peak. In our study on ion chromatographic separation of REE employing Ion Pac CS3 + CG3 column (sulfonic acid type) and tartaric acid (pH = 4.35) as eluent at 25 °C, Y together with Sc eluted after Gd and before Pr [13]. In the same system at 70 °C, Y eluted after Ho together with Gd, but this separation system as a whole was not very promising. When NTA was used as an eluent (pH = 2.7), the separation of heavy and middle REE was reasonable but Y coeluted with Eu (at 25 °C) or with Tb (at 70 °C) [13]. A partial separation of Y, La and Sc by anion exchange IC with in-column complexation with EDTA was reported by Nitsch et al. [22].

While RP-HPLC systems employing anionic surfactants as IIR and α -hydroxycarboxylic acids as components of the mobile phase were widely used for REE separation as an alternative to IC methods, the analogous systems with C₁₈ column plus cationic surfactant seem to be overlooked or forgotten. The early attempt to exploit this approach with the use oxalic acid as an eluent [23] in which however, yttrium coeluted with terbium, was not continued.

To the best of our knowledge, NTA was never used before for REE separation by anion exchange mechanism. In the present study a new method for selective separation of yttrium from all REE by RP-HPLC with tetra-*n*-butylammonium hydroxide (TBAOH) as IIR, buffered NTA solutions as eluents and UV/VIS detection with Arsenazo III, is described. In this system, at pH = 2.8–3.5 yttrium has an apparent atomic number (App.At.No.) of 61(1/2). (The App.At.No. is assigned according to the elution position of Y or Sc within the lanthanide series). Y is well separated from Nd (and also from Pm, which however does not occur in nature), as well as from Sm and heavier REE the latter treated as group. For lanthanides heavier than terbium the elution order does not follow the order of increasing ionic radii.

In selected elutions in which radioactive tracers were used, the effluent was collected in fractions and analyzed by γ -ray spectrometry to ascertain elution positions of individual REE including promethium.

2. Experimental

2.1. Chemicals

All reagents used were of analytical grade and used without further purification. All solutions were prepared in 18 M Ω cm water

obtained from a Milli-QRG ultra-pure water system (Millipore) and were deoxygenated with nitrogen.

The stock solution of 0.2 M NTA was prepared by weighing 9.56 g NTA (Sigma-Aldrich, Germany) and dissolving in water with the addition of 1 M NaOH in a 250 mL volumetric flask to achieve a clear solution of pH \sim 7. The solution of 0.4 M TBAOH (Acros Organics, USA) in water was used as the stock solution of TBAOH. The stock solution of 1 M NaCl was prepared by dissolving of 58.45 g NaCl (POCh, Poland) in water in a 1000 mL volumetric flask. At the early stage of our work we used stock solutions (1000 mg L⁻¹) of the REE's studied prepared by dissolution of their respective oxides (CeO₂, Eu₂O₃, Ho₂O₃, La₂O₃, Lu₂O₃, Nd₂O₃, Pr₂O₃ – Koch-Light Laboratories Ltd, UK – 99.99%; Dy₂O₃, Er₂O₃, Sc₂O₃, Tb₂O₃, Tm₂O₃, Yb₂O₃, Y₂O₃ – Johnson Matthey Ltd, UK – 99.99%; Gd₂O₃, Sm₂O₃ – Fluka AG, Switzerland – 99.99%) in HNO₃ and dilution with 18 M Ω cm ultra-pure water. For later experiments we used standard solutions (1000 mg L⁻¹) of all REEs studied (Chem-Lab NV, Zedelgem, Belgium–99.99%).

All eluents applied in the experiments were prepared by appropriate dilution and mixing of stock solutions of the eluent components to necessary concentrations with 18 M Ω cm ultra-pure water and then adjusting to required pH with HCl or NaOH. The post-column complexing reagent solution contained 0.12 M Arsenazo III and 0.5 M CH₃COOH, pH = 2.61. The solution was prepared by dissolving 0.093 g Arsenazo III and 28.5 mL glacial CH₃COOH (all from Fluka, Switzerland) in water in a 1000 mL volumetric flask.

Radioactive isotopes ⁴⁶Sc, ¹⁷⁷Lu, ¹⁶⁹Yb, ¹⁷⁰Tm, ¹⁷¹Er, ¹⁶⁶Ho, ¹⁶⁰Tb, ¹⁵²Eu, ¹⁵³Sm, ¹⁴⁷Nd, ¹⁴²Pr, ¹⁴¹Ce and ¹⁴⁰La were prepared by dripping of REE oxide solutions containing: Sc–50 μ g, Lu–20 μ g, Yb–30 μ g, Tm–50 μ g, Er–100 μ g, Ho–20 μ g, Tb–200 μ g, Eu–50 μ g, Sm–20 μ g, Nd–3 mg, Pr–30 μ g, Ce–4.2 mg in polyethylene ampoules, evaporating at 90 °C and irradiating for 50 min. in the reactor MARIA in Świerk (Poland) at a thermal neutron flux density of 1.0×10^{14} n cm⁻² s⁻¹. Promethium isotopes were formed during irradiation of Nd by the reactions: ¹⁴⁸Nd(n, γ)¹⁴⁹Nd \rightarrow β^- \rightarrow ¹⁴⁹Pm, and ¹⁵⁰Nd(n, γ)¹⁵¹Nd \rightarrow β^- \rightarrow ¹⁵¹Pm, respectively. After cooling for ca. 4 h. up to 2 weeks (for various isotopes), the tracers were washed out with 6 M HCl. Solutions of isotopes selected for experiments were evaporated and added to REE mixture injected onto the column.

2.2. Apparatus and procedure

The Dionex ICS-5000 SP-5 ion chromatograph (Thermo Fisher Scientific Inc. USA) was used in the investigations. The ion chromatograph was equipped with an Dionex ICS VWD UV-visible detector and Thermo Scientific conductivity detector. Separations were performed on an Kromasil 100 C₁₈ reversed-phase column. The individual REE's were separated by isocratic elution using nitrilotriacetic acid (NTA) as the complexing agent in the eluent and tetra-*n*-butylammonium hydroxide (TBAOH) as IIR. In some elutions NaCl was added to the eluent solution. Aqueous solutions of eluents containing appropriate concentrations of NTA, TBAOH and NaCl were prepared, and the required pH of eluent solutions were adjusted with HCl or NaOH. Before each run the whole chromatographic system was left to stabilize thermally for 30–45 min. Selected mixtures of standard solutions chosen from among the REE's studied were prepared by appropriate dilution and mixing of stock solutions. The standards were evaporated three times with the eluent solution, dissolved in known volume of the same eluent and injected onto the column.

Injections were performed manually with a Tefzel sample loop (Dionex).

The eluted REE were monitored by means of a Dionex ICS VWD UV-visible variable wavelength detector after they had undergone

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