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Chromatographic separation of thulium from erbium for neutron capture cross section measurements—Part I: Trace scale optimization of ion chromatography method with various complexing agents

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Abstract The impact of various ion chromatography parameters on the separation of trace amounts of thulium from erbium was examined to address the need for the preparation of a ^{171}Tm target for neutron capture cross section measurements. The following optimal operation parameters for analytical scale separations with cation exchange resin were established based on a modified separation resolution: 0.046 M α-HIB^{-} as eluent with a flow rate of 1.2 mL min^{-1} at 25 °C. Different carboxylic acids with varying pH were also investigated, which reaffirmed the use of α-hydroxyisobutyrate as the most suitable complexant for the separation of these neighboring lanthanides.

Keywords Thulium · Erbium · Ion chromatography separation · Hydroxyisobutyric acid

Introduction

The measurement of neutron capture cross sections for many actinide and lanthanide isotopes is crucial to the National Nuclear Security Administration (NNSA) and the weapons laboratories mission of science based stockpile stewardship [1, 2]. Lanthanide isotopes were commonly used as radiochemical detectors during nuclear weapons testing in order to obtain a detailed interpretation of post-detonation performance. Additionally, the neutron capture cross sections for many lanthanide isotopes are relevant to astrophysics to facilitate an improved understanding of elemental production in stars due to their vital role as branching point nuclei in the s-process [3]. These branching points are critical in understanding the isotopic abundance of elements in the universe and the neutron density in stars [4]. Hence, accurate measurements are required for numerous lanthanide isotopes, which either have not been investigated in the past or have high uncertainties associated with the currently reported neutron capture cross section values. One of these lanthanide isotopes of interest is ^{171}Tm ($t_{1/2} = 1.92$ a).

To obtain sufficient quantities of target material for a cross section measurement, this thulium isotope can be produced through neutron irradiation of isotopically enriched ^{170}Er (stable, 14.91 % abundance), following the reaction-decay scheme of $^{170}\mathrm{Er}(\mathrm{n},\gamma)^{171}\mathrm{Er}(t_{1/2} = 7.52$ h, beta-decay)^{171}Tm. An estimate of the production rate for ^{171}Tm after 50 days of irradiation with a neutron flux of 2×10^{15} n cm^{-2} s^{-1} indicates a sample (^{170}Er) to product (^{171}Tm) mass ratio of 27 [5]. After irradiation, the thulium will require separation from the excess erbium material in order to prepare the ^{171}Tm target for subsequent measurements. Although the short half-life of ^{171}Tm can pose difficulties in performing such measurements, the Detector for Advanced Neutron Capture Experiments (DANCE) located at the Los Alamos Neutron Science Center (LANSCE) at Los Alamos National Laboratory (LANL) allows for accurate neutron capture cross section measurements with only a few milligrams of target material [6]. In support of such an experiment, a ^{171}Tm target with more than 99 % isotopic purity is required. Thus, a highly

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efficient method for the separation of small quantities of thulium (1–10 mg) from a large excess of target material of the neighboring lighter lanthanide, erbium, is necessary.

The lanthanide chemistry across the series follows a periodic trend established by the decrease in ionic radii with an increase in the atomic number and a common oxidation state in solution. However, several of the lanthanides do exhibit other oxidation states in solution, +2 (Sm, Eu, Yb) and +4 (Ce), that result from the stability associated with an empty, half-filled and completely filled 4f orbital. The predominantly trivalent lanthanide chemistry is governed by cation–anion, ion–dipole and ion–induced dipole interactions leading to strong ionic interactions between the lanthanides and hard-sphere donor ligands (e.g. oxygen). Due to the labile nature of the lanthanide complexes, chromatographic techniques have become the method of choice for analytical and preparative scale separations. There is an extensive amount of literature available on the intragroup as well as intergroup separation of lanthanides elements and several in-depth reviews on this topic have been published [7–10].

The first detailed separation study of lanthanides by cation exchange resin with ammonium α-hydroxyisobutyrate (α-HIB) was carried out by Choppin and Silva [11]. This work formed the foundation for a large number of experiments [5, 12–28] performed over the next 50+ years utilizing α-HIB as the complexing agent with the primary source of complexant being α-hydroxyisobutyric acid (α-HIBA). However, earlier work by Mayer and Freiling [29] separated Sm–Eu and Eu–Tb pairs with different complexing agents (citrate, EDTA, lactate, glycolate and malate). Additionally, a study [15] in the early 1970s explored various α-hydroxycarboxylic acids as eluting agents with promising results in the separation of neighboring lanthanides, Nd/Pm, with α-hydroxy-α-methylbutyric acid (α-H-α-MBA) in the elution matrix. Since then, similar studies have been reported [30, 31]. With the introduction of post-column reagent systems [32] and improvements in chromatographic instrumentation in the 70 and 80s, group lanthanide separation methods for analytical purposes have been established [17–21, 23, 26–28]. However, only a limited number of these publications focused on the separation of neighboring lanthanides, specifically thulium from erbium, on a preparative scale [5, 22, 24, 25]. Although the same complexant, α-HIB, and cation exchange chromatography is employed in all of these methods, the experimental procedures and results vary drastically. Reported separations ranged from 95 % purity up to 99.6 % purity of the thulium fraction with relatively high recovery yields.

In an effort to develop a suitable separation method for neighboring lanthanides to address the need for obtaining a few milligrams of ^{171}Tm target material for neutron capture cross section measurements at DANCE, this work provides the results of analytical scale studies for the partitioning of these lanthanides prior to scale-up to preparative scale separations [33]. Experiments have been conducted with stable thulium and erbium to investigate the effects of eluent composition including different complexants, temperature and flow rate on the separation of these lanthanides through the use of an ion chromatography (IC) system equipped with an analytical cation exchange column.

Experimental

Reagents and lanthanide standards

All chemicals used were purchased as the highest purity available from Sigma-Aldrich: glacial acetic acid (99.99+ %), ammonium hydroxide (>99.99 %), 2-hydroxyisobutyric acid (99 %, α-HIBA), 2-hydroxy-2-methylbutyric acid (98 %, α-H-α-MBA), 2-hydroxy-3-methylbutyric acid (99 %, α-H-3-MBA), 2-ethyl-2-hydroxybutyric acid (99 %, α-E-α-HBA), 2-hydroxy-2-phenylacetic acid (99 %, α-H-α-PAA, mandelic acid) and lithium hydroxide monohydrate (>98.0 %). NIST traceable lanthanide standards (Er and Tm) of 1000 ppm in 5 % HNO_3 were purchased from GFS Chemicals. Whenever necessary these standards were diluted with ultra-pure HNO_3 purchased from Seastar Chemicals. The post-column reagent, 4-(2-pyridylazo)resorcinal (PAR), was purchased directly from Dionex and used as received. Calibration standards of pH 2, 4, 7 and 10 were purchased from VWR.

General procedures for sample preparation and measurement on the ion chromatography system

A Dionex ICS-3000 automated IC system was used for all the studies reported here. This instrument is equipped with an AS40 autosampler that uses a positive displacement sampling technique. The autosampler automatically filters each sample during loading by passing it through a 20 µm filter on the sample vial cap. The IC system is based on a gradient pump with up to four different eluent lines and utilizes a photodiode array detector (PDA-1) capable of measuring absorbance in 190–800 nm range. The instrument also has a post-column pneumatic controller that delivers a colorimetric reagent (post-column reagent) to the system. The cation exchange column used for this work was an IonPac CS3 4 × 250 coupled with an IonPAC CG3 4 × 50 guard column. The column has an ion exchange capacity of about 30 µeq/column. The guard column contains the same material as the main column; thus, it increases the overall retention time by 20 %.

The general procedure for sample preparation and measurements was adopted from Technical Note #23 published by Dionex [20]. The sample matrix consisted of 5 % HNO_3. A sample loop of 25 μL was used for all measurements and the total sample size for the autosampler was of 0.5 mL. All operating parameters were controlled through the Chromeleon software, except for the post-column pneumatic controller, which was controlled manually by adjusting the pressure to provide a certain flow rate as determined experimentally. The post-column reagent forms a 1:2 PAR:lanthanide complex with a very high formation constant [34]. Once the complex is formed in solution, the yellow color of the PAR solution without lanthanides turns red/orange. UV–Vis spectra of PAR with and without lanthanides, shown in Fig. 1, clearly show the shift in the absorbance band. This allows for the detection of lanthanides by analysis of the absorbance at 510 nm (independent of the specific rare earth metal in the complex) in comparison to the characteristic absorbance of PAR at 413 nm.

Data of absorbance vs elution time were analyzed with the Chromeleon software to obtain a retention time (t) for each peak of interest, area under each peak and full, left and right peak widths at 50 % ($w_{1/2}$), 10 % ($w_{0.1}$), 5 % ($w_{0.05}$) and base (w). Once these values were determined, a peak resolution or separation resolution (R) was calculated from:

$$R_s = \Delta t/(w_{2l} + w_1) \text{ where } \Delta t = t_2 - t_1, \tag{1}$$

where t_2 and t_1 correspond to retention times and $t_2 > t_1$, w_{2l} represents the left width of peak 2 and w_1 is the full peak width of peak 1. This modified separation resolution equation, Eq. 1, was tailored towards optimizing the purity of the first peak. Although different from the separation resolution established in traditional IC, similar adjustments have been made previously to account for non-Gaussian elution peaks [14]. Since the purity of the thulium fraction is critical to the separation procedure, the separation resolution was calculated using the left (Er, second peak) and full peak widths (Tm, first peak) at 10 and 5 % to emphasize the trailing edge of the thulium fraction into the leading edge of the erbium fraction, see Fig. 2. The right peak width of erbium was completely ignored, since it did not influence the purity or recovery of the thulium fraction. Additionally, an adjusted retention time, t'_R, for each peak was determined by subtracting the dead time from the measured retention time. Results presented in this work include error bars corresponding to the population deviation from triplicate measurements. For those studies where only duplicate measurements were made, only one set of values are presented with no error bars. The second set of measurements was run as a check to ensure trends from the first set were reproducible.

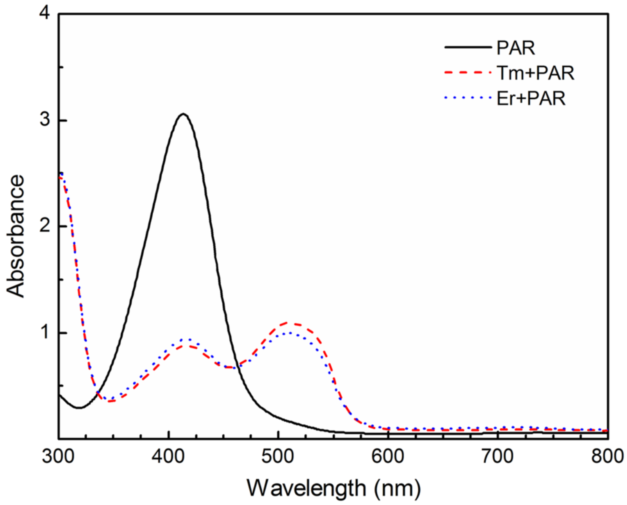

Fig. 1 UV–Vis spectra of PAR with and without thulium/erbium, shift in absorbance is independent of the individual lanthanide

α-HIBA concentration, temperature and flow rate optimization

The separation method as outlined in Dionex TN#23 [20] used two eluents, deionized water and 0.4 M α-HIBA (at pH ~4.6), where each eluent was set to a desired percent of the total flow rate using the gradient pump system. This method, which used 0.2 mM PAR, was adopted as the initial procedure for the separation of thulium from erbium on the IC system.

Even though the Dionex technical note preferred the use of a linear gradient for performing a lanthanide group

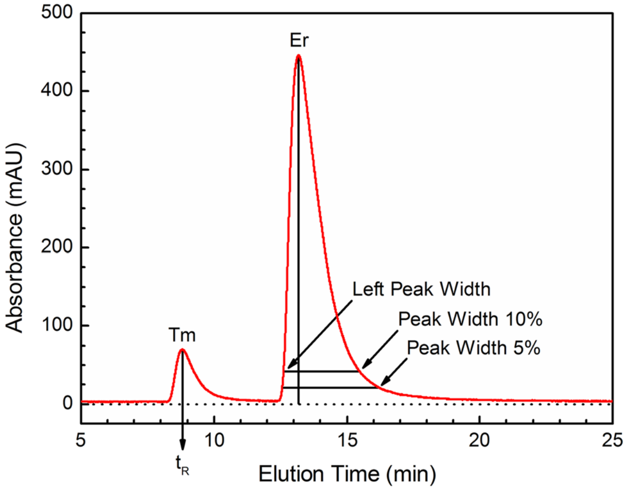

Fig. 2 Example of thulium and erbium separation chromatogram obtained from IC measurements where indicated peak widths represent values used for calculating the separation resolution as redefined in Eq. 1

separation, preliminary studies indicated separation of thulium from erbium to be more efficient with an isocratic elution. In order to determine the impact of α-HIBA concentration on the separation, measurements were made on the IC by varying the total flow rate percent of the 0.4 M α-HIBA eluent. The concentrations were varied from 0.048 to 0.08 M α-HIBA in 0.004 M increments. These measurements were performed using a mixture of 10 ppm Tm:100 ppm Er at 23 °C with an eluent flow rate of 1.000 mL min^{-1} and a post-column flow rate of 0.65 mL min^{-1}. The post-column flow rate was determined by volumetric measurements of the solution collected from the pneumatic controller at ~40 psi. A higher concentration of thulium and erbium in solution (25 ppm Tm:250 ppm Er) was used for the measurements at very low α-HIBA concentrations (0.052 and 0.048 M), where longer retention times resulted in broader elution peaks. Duplicate measurements were made at each given condition to ensure reproducibility of the results.

The influence of temperature on the separation resolution was investigated by measuring thulium and erbium samples of 10 ppm Tm:100 ppm Er with a 1.000 mL min^{-1} flow rate of 0.056 M α-HIBA eluent and the same post-column flow rate as before, 0.65 mL min^{-1}. Since the temperature control chamber on the IC unit was capable of achieving temperatures between 15 and 40 °C, duplicate measurements were made from 15 up to 40 °C in 2.5 °C increments (±0.2 °C).

The temperature study was extended beyond the capabilities of the Dionex ICS-3000 system. An addition of 120 cm long (0.010 in ID) PEEK tubing followed by the guard and the analytical columns were submerged in a temperature controlled circulating water bath, Blue M Electric WB-1110A. A digital temperature controller was utilized that allowed for adjustments from 5 °C above ambient temperature to 90 °C (±1 °C). The measurements were performed at a 1.200 mL min^{-1} flow rate of 0.056 M α-HIBA eluent with the post-column flow rate at 0.65 mL min^{-1} and included two different concentrations of lanthanide samples: 10 ppm Tm:100 ppm Er (all temperatures) and 33 ppm Tm:333 ppm Er (50–90 °C only).

To determine the flow rate dependency on the separation, the eluent flow rate was varied from 0.400 up to 1.800 mL min^{-1}. Above 1.800 mL min^{-1}, the backpressure at the column was very high (>4000 psi) causing the tubing connection at the column to fail. Once again, duplicate measurements were made at each setting with 10 ppm Tm:100 ppm Er sample solutions at 25 °C using 0.056 M α-HIBA eluent composition and the same post-column flow rate as before.

Reproducibility and increase in sample mass-load

Once the optimum conditions with respect to α-HIBA concentration, flow rate and temperature were determined, studies were carried out in order to ensure the measurements were accurate and reproducible. Sample solutions of 10 ppm Tm:100 ppm Er were analyzed with the IC using these following conditions: flow rate at 1.200 mL min^{-1}, temperature at 25 °C, 0.056 M α-HIBA, post-column flow rate at 0.65 mL min^{-1}. The temperature control chamber that housed the column was equilibrated at least 6 h prior to making any measurements. Then identical samples were analyzed over several hours and another ten identical samples a few days later.

Lastly, analytical scale separations were performed using the optimized parameters with two different sets of thulium and erbium solutions: 10 ppm Tm:100 ppm Er and 100 ppm Tm:900 ppm Er. Individual thulium and erbium standards were analyzed along with the mixed samples in order to determine the recovery yields. Triplicate measurements were made for these two different sample solutions.

Separation dependency for different complexants with varying pH

In addition to α-HIBA, four other 2-hydroxycarboxylic acids were investigated as possible eluents for the separation of thulium from erbium. These complexants and their corresponding pK_a values are presented in Fig. 2. Provided with the optimal concentration of α-HIBA as 0.056 M, it was taken as the starting point for the pH dependency studies with these other complexants. The pH of the solution was continuously increased in small increments (between 0.1 and 0.2) through addition of $\text{LiOH·H}_2\text{O}$ until the elution peaks started overlapping (~6 min retention time for Er) or the equivalence point was reached with respect to the deprotonation of the entire α-HIBA in the matrix. The same procedure was used to obtain the pH dependency results for the other carboxylic acids as summarized in Fig. 3. Triplicate measurements were made at each individual pH.

In addition to varying the pH, IC separation measurements were made by holding the pH constant and varying the concentration of the α-hydroxycarboxylic acid. This study was performed only for α-HIBA. The starting concentration of α-HIBA was 0.056 M at $\text{pH} = 4.63$, where the pH was held close to 4.63 ± 0.01 and the α-HIBA concentration was varied from 0.056 up to 0.060 M. Triplicate measurements were made for each elution system. Standard pH measurement techniques were utilized for pH determination of the experimental

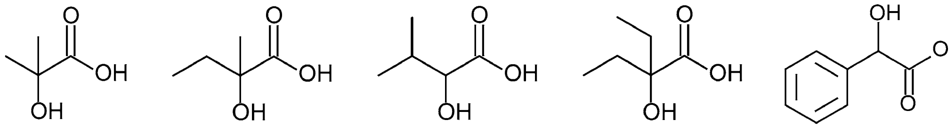

Fig. 3 Different carboxylic acids used as complexants (from *left* to *right*): 2-hydroxyisobutyric acid (α-HIBA, pK_a of 3.70–4.00), 2-hydroxy-2-methylbutyric acid (α-H-α-MBA, pK_a of 3.70–3.73), 2-hydroxy-3-methylbutyric acid (α-H-3-MBA, pK_a of 3.87–3.89), 2-ethyl-2-hydroxybutyric acid (α-E-α-HBA, pK_a of 3.58–3.64) and 2-hydroxy-2-phenylacetic acid (α-H-α-PAA, pK_a of 3.10–3.35). All pK_a values adopted from [35]

solutions. The measurements were performed using the sympHony Series pH Electrode with AglAgCl internal reference system coupled with the sympHony Meter SB70P.

Results and discussion

Optimizing the IC parameters for Tm/Er separation

Initial studies were focused on optimizing operating parameters such as eluent composition (using the two eluent system), flow rate and temperature for the general procedure adopted from Dionex Technical Note #23 [20]. These parameters were optimized to achieve a good separation resolution, R_s. At the same time it was attempted to keep the adjusted retention times, t'_R, as low as possible to reduce the volume of thulium elution fraction and analysis time. The dependency of these factors on eluent composition, flow rate and temperature is presented in Fig. 4.

The dependency on eluent concentration was exactly as expected. A decrease in the α-HIBA concentration resulted in a linear improvement of R_s with an exponentially increasing t'_R. This occurs because the trivalent lanthanide ions interact with the conjugate base of α-HIBA (α-HIB$^-$) to form a single, positively charged or neutral complex, which lowers its affinity for the cation exchange resin. Although separation appeared to improve at lower α-HIBA concentrations, it also resulted in longer retention times and wider elution bands. Since the goal was to minimize the thulium elution fraction and maximize the separation resolution, 0.056 M α-HIBA was selected as the ideal eluent concentration, leading to t'_R of ~7.5 and ~12 min for thulium and erbium, respectively. A similar analysis was performed with regards to temperature and flow rate dependency. An optimal temperature of 25 °C (from the initial 15–40 °C study) was selected along with an elution flow rate of 1.200 mL min^{-1} and a PAR flow rate of 0.65 mL min^{-1}. The extended temperature study up to 90 °C showed significantly higher separation resolution at temperatures above 70 °C; however, this also resulted in substantially longer retention times and broad elution peaks. Therefore, all other experimental measurements were performed at 25 °C.

Reproducibility and impact of increased mass-loading

Once the initial operating parameters were established, measurements were performed to examine the reproducibility of the separation. The results indicate excellent reproducibility for R_s and t'_R. Based on ten different measurements carried out each day for two different days, R_s values at 10 and 5 % peak widths appeared to have random fluctuations of <5 % from average and t'_R fluctuations, also random, were <3 % deviation from average. These results are significant in demonstrating the use of this IC method as a robust technique for performing separations in a continuous mode over a single day or for repeating the separations on a different day.

Under the optimum conditions established above, the separation was carried out for two different samples with varying lanthanide concentrations, 10 ppm Tm:100 ppm Er and 100 ppm Tm:900 ppm Er. Results from these experiments are summarized in Table 1. The measured separation resolutions match closely with those reported in literature [5]. As expected, the resolution and recovery yield of thulium decreased with increasing concentration of the lanthanides. At lower concentrations, thulium is completely separated from erbium, but at the higher concentrations almost 9 % of the thulium was lost in the erbium fraction. The decrease in thulium recovery is a direct result of an increase in the thulium elution peak width due to the larger mass loading. The purity of the thulium fraction could not be determined due to the inability of PAR to distinguish between different lanthanides, as mentioned earlier. The separation of lanthanides from PAR and subsequent analysis of the lanthanides content with atomic emission spectroscopy is addressed in Part II of this work [33].

Different complexants and pH dependency

Out of the five different α-hydroxycarboxylic acids investigated as complexants for the chromatographic elution of thulium and erbium, only α-HIBA and α-H-α-MBA were able to elute these lanthanides off the cation exchange column within 45 min of elution using operating

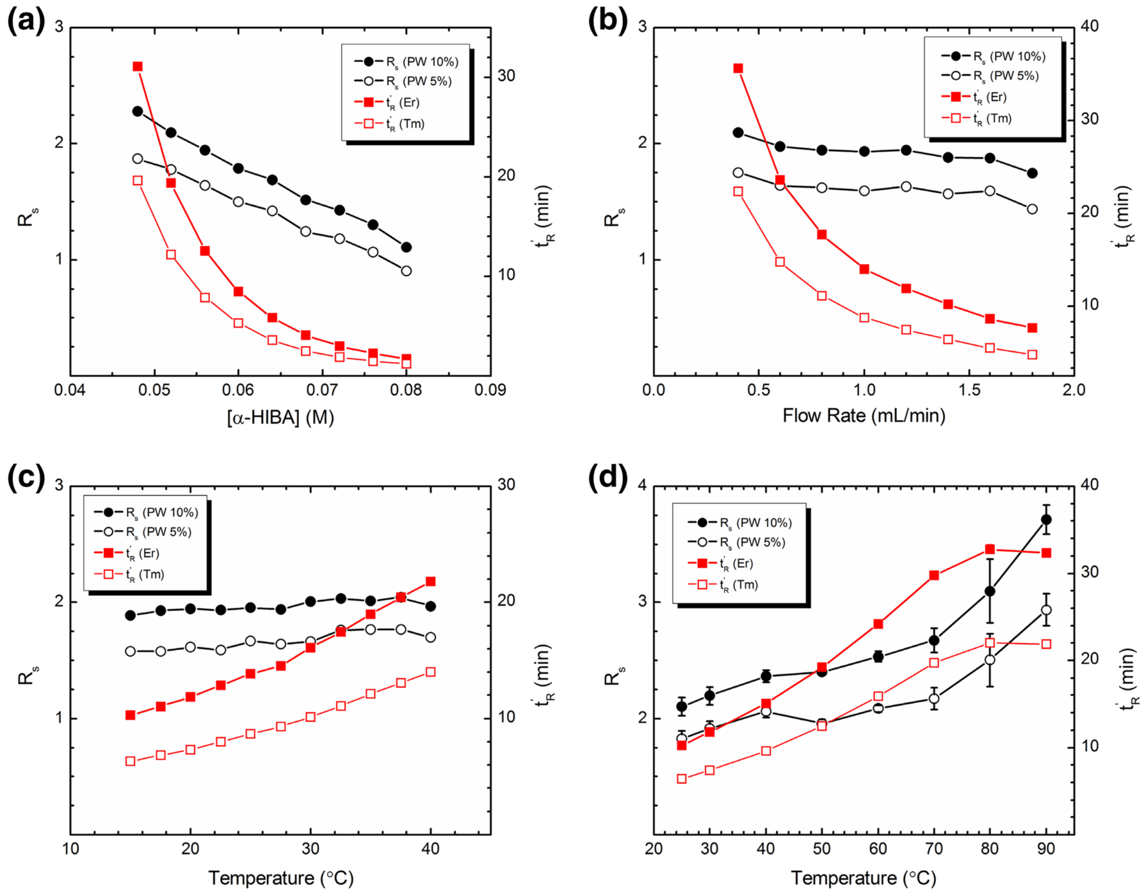

Fig. 4 Effects of [α-HIBA] (**a**), eluent flow rate (**b**) and temperature between 15 and 40 °C (**c**) and 25–90 °C (**d**) on the separation resolution, R_s, for peak widths (PW) at 10 and 5 % and on adjusted retention time, t'_R, for erbium and thulium. Operating conditions: 10 ppm Tm:100 ppm Er, eluent flow rate of 1.000 mL min^{-1} (**a**, **c**) and 1.200 mL min^{-1} (**d**), temperature at 23 °C (**a**) and 25 °C (**b**), 0.056 M α-HIBA for (**b–d**) and PAR flow rate of 0.65 mL min^{-1}

Table 1 Separation of thulium from erbium in two different samples of varying lanthanide concentrations

Tm:Er (ppm)	R_s (PW %)	Recovery yield (%)
10:100	1.84 ± 0.07 (10 %)	Tm: 101.4 ± 1.2
	1.53 ± 0.06 (5 %)	Er: 99.5 ± 0.2
100:900	1.49 ± 0.09 (10 %)	Tm: 91.3 ± 0.6
	1.19 ± 0.07 (5 %)	Er: 101.8 ± 1.0

parameters as established previously. The results from the pH dependency study at constant α-HIBA concentration as well as from an investigation of the α-HIBA concentration dependency at constant pH on R_s and t'_R are presented in Fig. 5 as a function of the conjugate base concentration, α-HIB^-. This concentration was calculated from the Henderson-Hasselbalch equation using measured pK_a values (α-HIBA as 3.86 ± 0.03 and α-H-α-MBA as 3.84 ± 0.04). The elution results from this study are similar to those obtained in previous experiments with the two-eluent system, DI-water and 0.4 M α-HIBA. However, in the previous experiments, both the α-HIBA and the pH were varied simultaneously, so it was more difficult to understand how each factor individually affects the elution, see Fig. 4. Almost all published literature work on the topic of lanthanides separation with IC state that the pH of an elution system is considered to be the major factor influencing the separation. However, the results in Fig. 5 clearly indicate that R_s and t'_R are only dependent on the conjugate base concentration of the complexant. This is not surprising at all, since the elution process is due to the formation of the lanthanide complexes with the conjugate base, in this case α-HIB^-. Therefore, the elution is not directly dependent on the pH. Instead it is the resulting conjugate base concentration in a solution containing a given amount of complexant at a given pH that determines the elution parameters, R_s and t'_R. The results show an increase in R_s with decreasing α-HIB^- concentration, where the rate of increase is not linear. There appears to be a plateau around

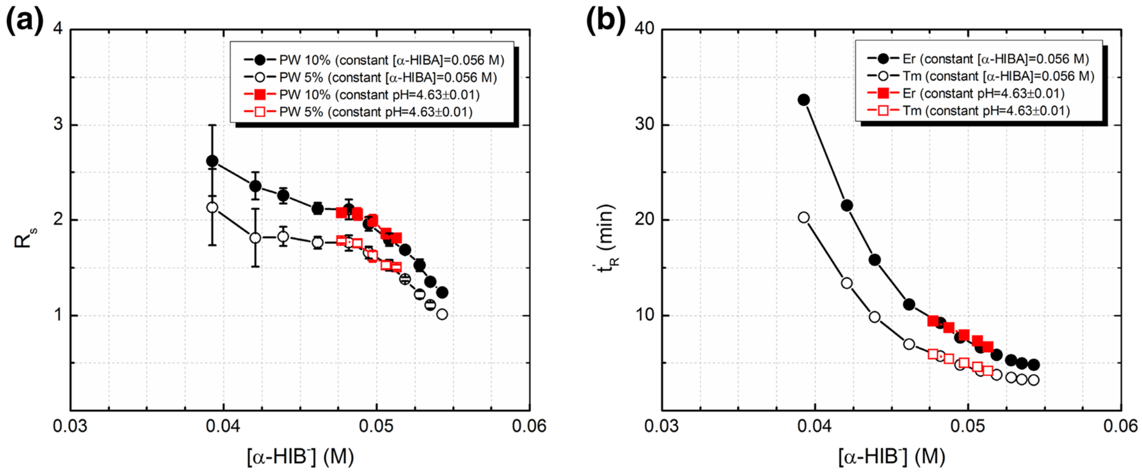

Fig. 5 Dependency of pH at constant [α-HIBA] (0.056 M) and of [α-HIBA] at constant pH (4.63) on the separation resolution (**a**), R_s, for peak widths (PW) at 10 and 5 % and adjusted retention time (**b**), t'_{R}, for erbium and thulium represented as a function of the conjugate base concentration

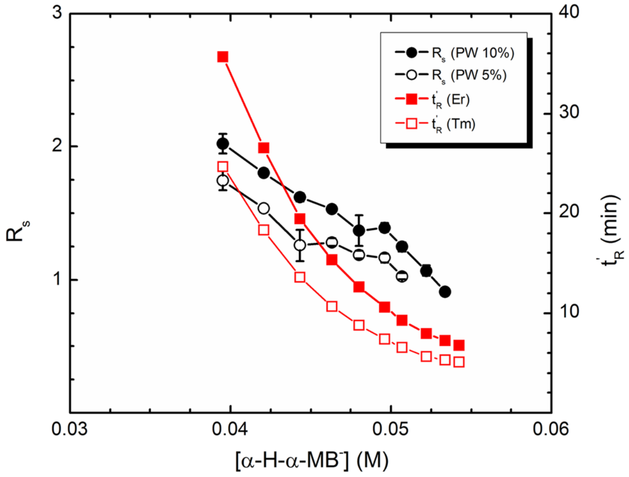

Fig. 6 Dependency of pH at constant [α-H-α-MBA] (0.056 M) on the separation resolution, R_s, for peak widths (PW) at 10 and 5 % and adjusted retention time, t'_{R}, for erbium and thulium represented as a function of the conjugate base concentration

0.045 M α-HIB$^-$ but this feature is not present in the measured t'_{R} plot. The t'_{R} follows an exponential decrease with increasing α-HIB$^-$ concentration, which is expected. Independent of pH dependency at constant α-HIBA concentration or α-HIBA concentration dependency at constant pH, both elution parameters R_s and t'_{R} show complete overlap when plotted as a function of α-HIB$^-$. Thus, either complexant concentration or pH adjustments can be made accordingly to accomplish the desired R_s and t'_{R}.

A similar study was performed for the α-H-α-MBA elution system, but only the pH dependency at constant α-H-α-MBA concentration was investigated, Fig. 6. It is assumed that the same conjugate base behavior as observed for α-HIBA system applies to this acid. The trends for both R_s and t'_{R} follow closely with those obtained for the α-HIBA elution. For comparison purposes, R_s at peak width of 10 % and t'_{R} of thulium from each acid system are provided in Fig. 7a as a function of their corresponding conjugate base concentrations. The results suggest a lower R_s for α-H-α-MBA at a given conjugate base concentration in comparison to α-HIBA, although the t'_{R} behavior is the opposite. Looking back at the definition of R_s, Eq. 1, and the results presented here, it can be concluded that the peak widths for α-H-α-MBA elution are wider than those for α-HIBA, which is exactly what is observed in the raw data, Fig. 7b. This is evidence that the α-H-α-MBA elution system is far less suitable for the thulium/erbium separation in comparison to α-HIBA, which has narrower elution peaks, lower retention times and higher separation resolution. Results of similar studies in literature are not as complete. A paper by Schwantes et al. [5] only provides results for pH vs α-HIBA but does not include any data for α-H-α-MBA. In other publications, comparison between these two acids are made at constant pH [15], showing α-H-α-MBA to be almost as good for the separation of heavier lanthanides as α-HIBA. In another work [31], α-H-α-MBA is shown to perform poorly for the separation of heavier lanthanides in comparison to α-HIBA. However, both of these articles show that α-H-α-MBA is better for the separation of neighboring light lanthanides (up to cerium). The work by Raut et al. [31] also includes data for a comparison of retention times with varying pH (only for lanthanum, neodymium, gadolinium and lutetium). The relative trends in that work are comparable to those presented in this paper for thulium and erbium.

Experiments with the other three α-hydroxycarboxylic acids resulted in no elution of thulium/erbium within an hour even though their formation constants are comparable

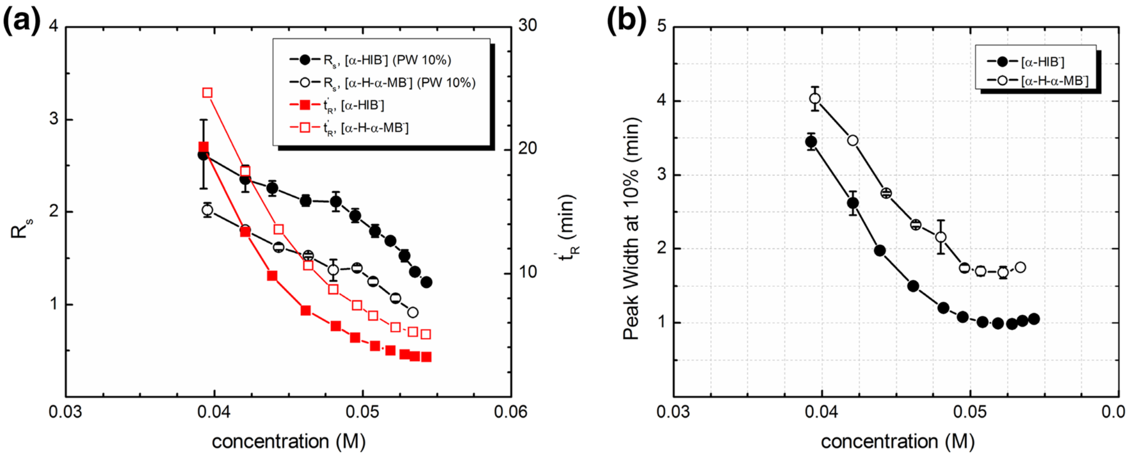

Fig. 7 Comparison of the separation resolution (**a**), R_s, for peak widths (PW) at 10 % and adjusted retention time, t'_R, for thulium as a function of the conjugate base concentration for two different α-hydroxycarboxylic acid elution systems: α-HIBA and α-H-α-MBA, data adopted from Figs. 5 and 6. Comparison of the thulium peak widths at 10 % (**b**) as a function of conjugate base concentration for the same two α-hydroxycarboxylic acids

Table 2 Formation constants of erbium and thulium complexes with four different α-hydroxycarboxylic acids, data adopted from [35]

Acid	Er			Tm		
	logβ_1	logβ_2	logβ_3	logβ_1	logβ_2	logβ_3
α-HIBA	3.01–3.07	5.54–5.70	7.56–7.80	3.05–3.13	5.15–5.79	7.71–7.84
α-H-α-MBA	3.32	6.05	8.03	3.37	6.13	8.05
α-E-α-HBA	3.11	5.27	6.60	–	–	–
α-H-α-PAA	2.68–3.15	5.41	–	2.71–3.20	5.56	–

to α-HIBA and α-H-α-MBA, see Table 2. These formation constants for 1:1 (logβ_1), 1:2 (logβ_2) and 1:3 (logβ_3) complexes between the lanthanides and the conjugate base of the α-hydroxycarboxylic acids are adopted from an IUPAC report published in 2003 [35] with no data available for α-H-3-MBA. The reason for no observed elution of the lanthanides with α-H-3-MBA, α-E-α-HBA or α-H-α-PAA is likely driven by the kinetic hindrance of the extra methyl/ethyl/phenyl group that significantly delay the complexation with the lanthanides.

Conclusions

This manuscript establishes the analytical scale separation parameters for isolating a high purity fraction of thulium from excess erbium with maximum recovery yield. The standard separation resolution definition was redefined to emphasize the purity aspect of the thulium sample. The reproducibility of utilizing an automated ion chromatography system, Dionex ICS-3000, as well as the impact of mass loading was verified through experimental measurements. Even though five different carboxylic acids were examined, it is clear that α-hydroxyisobutyrate is the complexant of choice for cation exchange based chromatographic separation of these lanthanides. The operational parameters established in this work were subsequently implemented as the starting point for preparative scale separations detailed in Part II of this manuscript series.

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