Determination of REEs, Th, and U in Seawater after Off-Line SPE by ICP-MS

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Preface

This master project was performed at the Department of Chemistry at the University of Oslo, under the supervision of Grethe Wibetoe and Dejene Kifle.

I am grateful to the Department of Chemistry for providing me with this opportunity. To my supervisors; thank you for your teaching, guidance, and constructive feedback during my master period. I thank Anne-Marie Skramstadt and Muhammad Ramzan for technical support and advice. I also extend my gratitude to Tor Bjørnstad for his masterful insights, and Dag Øistein Eriksen for valuable support and feedback. The technical sales consultant from Phenomenex Inc., Kaja Lycke, deserves a special mentioning for exceptional customer service.

Finally, I thank my husband Sverre Larsstuvold Sand for his endless support, patience, and unfiltered evaluation of my work.

Oslo, Norway, May 2017

Sviatlana Varonina

Abstract

There is an increasing interest in determination of rare earth elements (REEs), thorium (Th), and uranium (U) in seawater. Inductively coupled plasma mass spectroscopy (ICP-MS) is generally considered the best choice for measurements of trace metal ions in aqueous samples. However, seawater matrix contains high concentrations of total dissolved solids (TDS) that cause system clogging, while concentrations of analytes are exceedingly low (ng/L range). Dilution of samples to circumvent high TDS is thus a non-viable option on its own. Determination of REEs, Th, and U in seawater therefore demands a pretreatment step that removes matrix cations and preconcentrates analytes to quantifiable levels. Off-line solid phase extraction (SPE) utilizing metal chelating resin is a simple, low-cost, applicable technique for removing matrix cations. However, there is still no well-established method for preconcentration and separation of REEs, Th, and U from seawater using off-line SPE. In this project a novel off-line SPE setup packed with Chelex® 100 chelating resin was developed. This SPE method successfully reduced TDS to that which was tolerable by ICP-MS, i.e., less than 0.2 %, and from samples of spiked artificial seawater recovery of REEs, Th, and U was equal to or exceeded 82 %. When working with trace metals in the ng/L range, proper rinsing of the ICP-MS system is crucial. Thus, a special rinsing procedure was also developed in this project. The resulting novel method for determination of REEs, Th, and U in seawater was applied to environmental samples from Fuengirola, Spain, and Oslo, Norway. Comparison between these analyses and measurements performed by other research groups using different methods, showed similar levels of trace elements. This strongly suggests that the method developed in this project is reliable. Being mobile, compact, and easy to manage, this SPE method therefore holds the potential to become a useful tool for both laboratory and field work.

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Abbreviations

CRM	Certified reference material
ICP	Inductively coupled plasma
ICP-MS	Inductively coupled plasma mass spectrometer/spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometer/spectrometry
IS	Internal standard
IUPAC	Union of Pure and Applied Chemistry
HSAB	Hard Soft Acid Base
LOD	Limit of detection
LOQ	Limit of quantification
REEs	Rare earth elements
SCX	Strong cation exchanger
SPE	Solid phase extraction
STD	Standard deviation
TDS	Total dissolved solids

1. Introduction

1.1. Interest, importance and challenges of the study

Rare earth elements (REEs) and the actinides thorium (Th) and uranium (U) are a group of metals consisting mainly of elements with atomic orbitals producing fundamental spectral lines (f-block elements of the periodic table). The concentrations of these metals in seawater vary significantly depending on geography. Extensive research was performed on their distribution in the 1960s, and the data obtained was used to create sets of concentration patterns, mainly for REEs [1, 2]. Such patterns can be used to investigate mixing of water masses, ocean floor events and anthropogenic changes [3]. These processes are of great interest, as they are linked to current global problems such as climate change and environmental pollution.

Obtaining information on concentration of REEs, Th, and U and their relative distribution in seawater is important for the study of environment and marine geochemistry. The global production of lanthanides and actinides, used in industry, medicine, and agriculture has increased from a few tons to hundreds of kilotons per year during the last 60 years [4]. The result is a potential risk to the environment, as their bioavailability and toxic properties are still under investigation [4, 5]. REEs are infamous worldwide as microcontaminants of natural water sources [6]. Consequently, the demand for collection of data on trace elements in seawater is increasing. Furthermore, there is a general interest in their oceanic cycling [3]. Obtaining patterns of trace elements will make it possible to predict the transport and fate of contaminants in the ocean. This will provide a basis for assessing the degree of pollution and protect the ocean environment.

Norway has one of the world's largest deposits of Th according to the report of the Thorium Committee in 2008 [7]. Minerals containing U are also present in the ground all over the country. High levels of these metals occur in costal seawaters due to weathering and erosion of the rocks containing them. Some REEs are used in catalytic converters in cars, i.e., there is a possible emission into the seawater in the areas where highways pass along the coastline.

Over the last 30 years, ICP-MS has been the method of choice for measurements of trace and ultratrace metal ions in aqueous samples. ICP-MS has excellent performance in terms of sensitivity, limit of detection (LOD), and multielement capability [4, 8].

However, determination of trace elements in seawater with ICP-MS is challenging. The matrix contains high concentrations of dissolved salts (about 35 g/L), causing system clogging during ICP-MS analysis. In addition, some components of seawater present at high concentrations (sodium (Na), magnesium (Mg), calcium (Ca), potassium (K), etc.) lead to signal suppression and other matrix interferences that cannot always be eliminated by internal standards (IS). Since the concentration of REEs, Th, and U in seawater are exceedingly low (ng/L range) dilution is not an option, as it will bring the concentrations of most or all of the analytes below the limit of detection (LOD). Finally, to obtain accurate and reliable results, spectral interferences must also be considered [3 – 5, 9].

There is still no well-established methods or guidelines describing analysis of REEs, Th, and U in seawater. In addition, the literature on the subject is sparse [10, 11]. Probable reasons are that method development requires time, manpower, and financing, and determination of REEs, Th, and U in seawater is not of high priority globally. Hence, only a few research groups in the world conduct experiments in this field. During the last 15 years, roughly 12 laboratories have conducted research on REEs, Th, or U in seawater [5, 12 – 23], seven of which are in Japan. However, only one research group, in the University of Plymouth (Devon, UK), used off-line SPE in their research [21]. Other research groups used chelating disk, on-line-, and batch method. Of all the methods, off-line SPE is less labour intensive and less time consuming. Moreover, it does not require large volumes of solvents and expensive, complicated instrumentation, as is the case for on-line SPE. Off-line SPE of REEs, Th, and U from seawater is thus particularly interesting.

1.2. REEs, Th, and U: General knowledge and occurrence in seawater

Rare earth elements are a group of 17 elements: 15 lanthanide elements, yttrium (Y), and scandium (Sc). Sc is not always classified as a rare earth element. However, The International

Union of Pure and Applied Chemistry (IUPAC) includes this element in their rare-earth element definition [24].

REEs are called rare historically, because most of them were originally isolated in the 18th and 19th centuries as oxides from rare minerals. These elements have chemical similarity, and efficient separation processes were thus developed as late as in the 20th century [25]. Most REEs are not as uncommon in nature as the name implies. In fact, promethium (Pr) is the only truly rare element. It has no stable isotopes.

REEs have relatively short residence times in the ocean, about 400 years. Most of REEs are brought to the oceans by rivers that derive REEs from the weathering of continental rocks. An additional source of REEs in the ocean is submarine, volcanic activity, although terrigenous input of REEs dominates [25]. All REEs except one behave similarly in seawater, by occurring in 3+ oxidation states. Cerium (Ce) is the only exception; it occurs in Ce^{4+} form and is highly insoluble. Therefore, Ce is depleted in seawater relative to the other REEs. Complexes with carbonate ion (CO_3^{2-}) are the dominating species of REEs complexes, e.g., $LaCO_3^+$ [26 – 29].

The elements U and Th display sharply contrasting geochemical behaviour. Uranium is dissolved in seawater as the stable uranyl carbonate species, $UO_2(CO_3)_3^{4-}$ [30]**.** U has a residence time in the oceans of about 400 000 years, while thorium, as Th^{4+}, is removed from solution with a residence time of less than 100 years. Both Th and U enter the ocean through weathering and erosion [30, 31]. The prevailing inorganic species of Th in seawater are hydroxy-carbonate complexes [32, 33].

1.3. Goals of the project

Solid phase extraction (SPE) has been successfully used for separation of trace metal ions from environmental water samples [34]. The focus of this project is the development of a simple off-line SPE-based method for preconcentration of specifically REEs, Th, and U in *seawater*, which constitutes water samples with high salinity. Thus, removal of matrix cations and preconcentration of analytes become two crucial objectives that must be adequately achieved. The novel SPE setup should also be mobile and compact to be applicable to fieldwork. SPE techniques like the batch method and the on-line method have already been

used for determination of REEs, Th, and U in seawater [14 – 20], but, as previously mentioned, they have considerable disadvantages: The batch method is more complicated-, and on-line methods require more advanced equipment than off-line methods. Off-line SPE methods are thus both less work-intensive and less costly, and as such of great interest.

2. Methods

2.1. SPE

2.1.1. SPE technique

SPE involves partitioning between a liquid and a solid phase. This type of extraction enables concentration and purification of analytes from a solution by adsorption on a solid sorbent. This technique is based on passing the liquid sample through a sorbent container, filled with sorbent that retains the analytes. After the sample has passed through the sorbent, retained analytes can be recovered with a suitable solvent. Concentration of the analyte is achieved by eluting the retained elements with a smaller volume of liquid than the sample volume.
SPE usually consists of four steps. The first step is conditioning: Conditioning solution, containing the same solvent as the analyte solution, is passed through the sorbent. This step wets the packing material, solvates the functional groups, and removes possible impurities initially contained in the sorbent. The second step is loading: The analytes, possibly with non-analytes, are retained. The third step is washing: This removes retained non-analytes while leaving analytes on the sorbent. The fourth step is elution: Analytes are eluted by a suitable solvent [9]. Figure 2.1 presents schematically the four SPE steps.

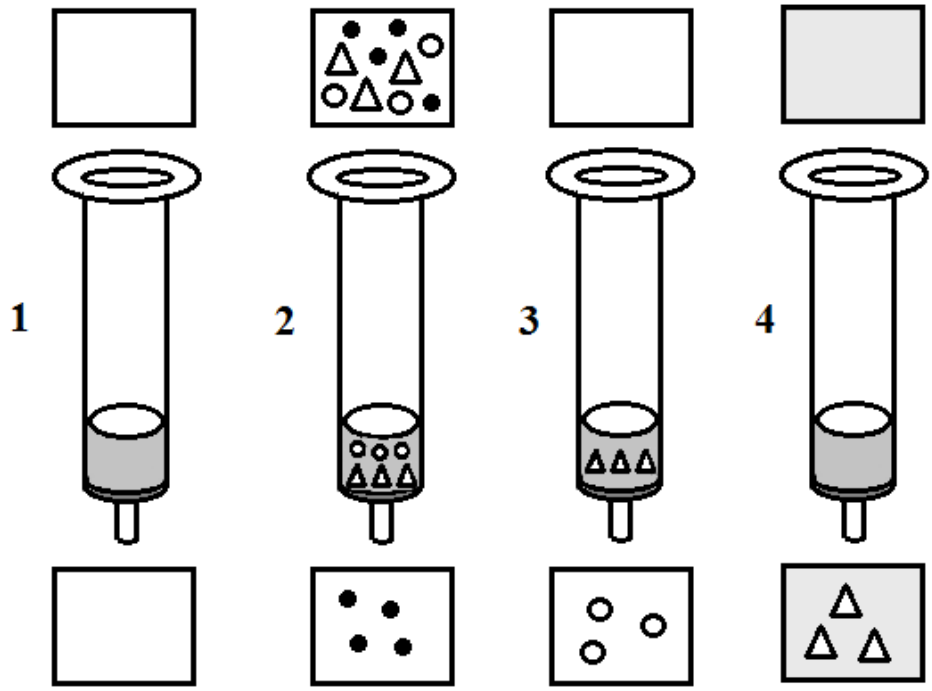

Figure 2.1. SPE steps: 1) Conditioning 2) Loading 3) Washing 4) Elution.

2.1.2. SPE types according to retention mechanisms

Preconcentration of trace elements requires adsorption on a solid sorbent. The mechanism of retention depends on the nature of the sorbent, and may include reversed phase, ion exchange, chelation, or a combination of the latter two.

Reversed phase

Reversed phase is a type of extraction when mid- or nonpolar analytes are adsorbed on nonpolar solid sorbents by van der Waals forces or hydrophobic interactions [9, 35].

Ion exchange

Ion exchange extraction is an exchange of analyte ions and counter-ions of a sorbent, i.e., ion exchange is based on electrostatic interactions. Anionic compounds are adsorbed on anionic exchangers, whilst cationic compounds are adsorbed on cationic exchangers [9, 35].

Chelation

Chelation is a type of extraction when ligands bind cations on two or more coordination sites, i.e., covalent interaction. Among the atoms possessing chelating properties are: Oxygen (O), nitrogen (N), sulphur (S), and phosphorous (P). From the nature of functional groups containing these atoms, the selectivity of each ligand towards each cation can be predicted [9, 36]. Cations can be divided into three groups according to the Hard Soft Acid Base (HSAB) theory (Figure 2.2). Hard acids form complexes with hard bases (O and N), soft acids form complexes with soft bases (S and P), and borderline acids form complexes with both hard- and soft bases. However, this grouping is not absolute, i.e., different oxidation states may belong to different categories. Example: Cr^{6+} may be grouped as hard while Cr^{3+} may be grouped as intermediate [36].

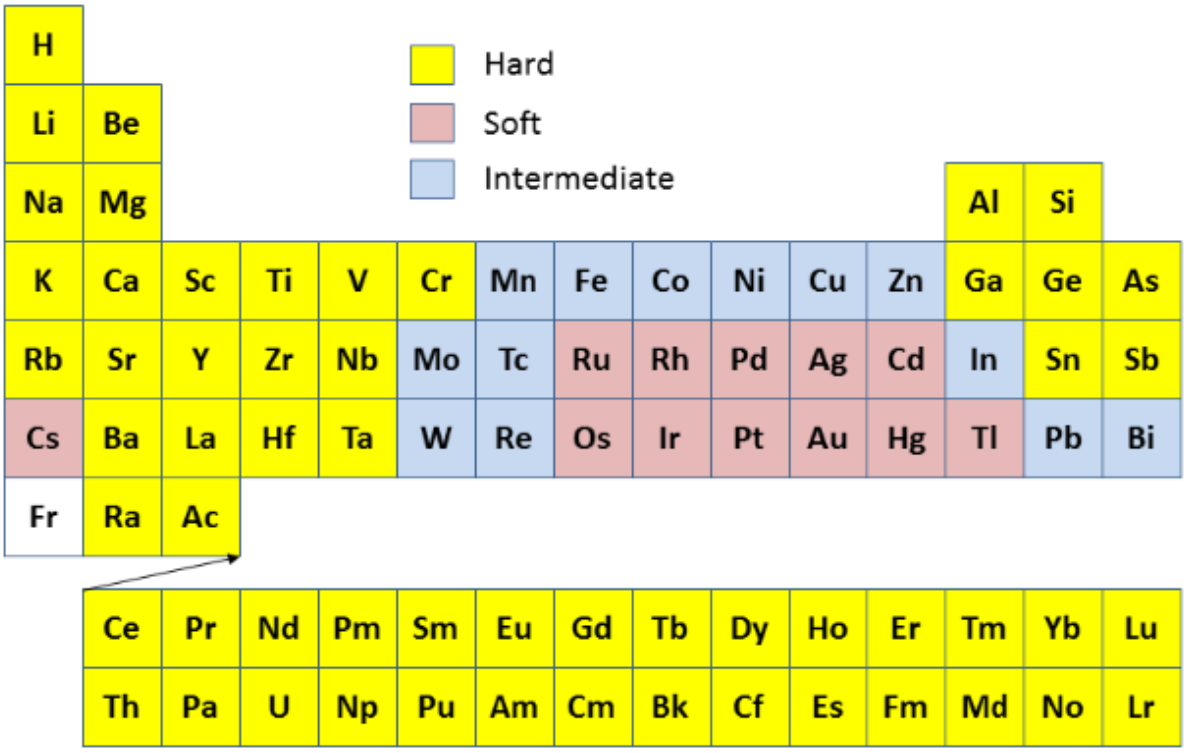

Figure 1.2. Approximate and rough grouping of hard, soft, and intermediate Lewis acids (figure is reproduced from Bjørnstad [36] with permission from the author).

2.1.3. Specialized ion exchange resins

Specialized ion exchange- or ion exchange chelating resin is a hybrid resin. It is an ion exchange resin that contains chelating groups. Hence, such resins have both ion exchange and chelating properties [9].

2.1.4. Sorbent containers

The sorbent can be packed into four types of containers, which are filled microcolumns, syringe barrels, cartridges, and discs (Figure 2.3).

The most popular sorbent containers for off-line SPE are cartridges and syringe barrels [9]. They are of high purity, easy to apply, and perfect for small volumes of samples. However, they have slow sample-processing rates and a low tolerance to clogging, because cartridges and syringe barrels have a small cross-section area [37]. In this project, syringe barrels are used.

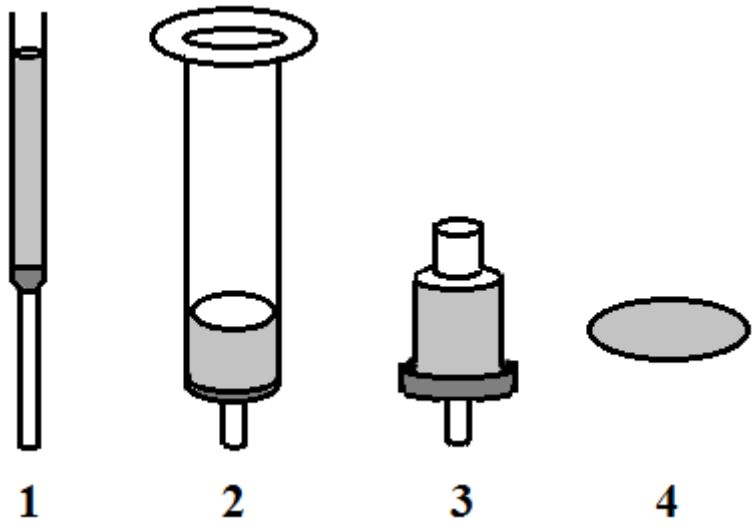

Figure 2.3. Sorbent containers: 1) Microcolumn 2) Syringe barrel 3) Cartridge 4) Disk.

2.1.5. SPE in this project

In this project, off-line preconcentration is used. Trace amounts of REEs, Th, and U are separated from seawater matrix cations. As the sample is an aqueous solution and the analytes

are all in ionic form, chelating resins are the best choice for selective separation of lanthanides and actinides (Figure 2.4) [35, 37].

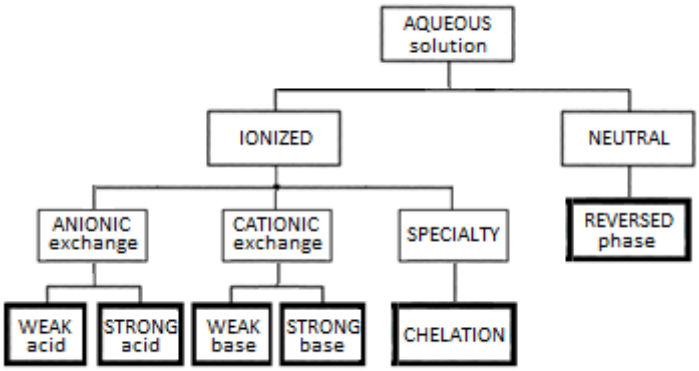

Figure 2.4. Method selection guide for choosing a suitable SPE phase for aqueous solutions.

One of the most popular ion exchange chelating resins for analysis of trace metals in natural water samples is Chelex® 100, produced by Bio-Rad Laboratories, Inc. (Berkeley, California, US) [38]. In the present project, Chelex® 100 was used. It is a styrene-divinylbenzene co-polymer containing iminodiacetic acid groups (Figure 2.5), which change their properties depending on pH. The selectivity of Chelex® 100 resin for metal cations corresponds to that of iminodiacetic acid. It is approximately 5000 times more selective for divalent over monovalent ions [39].

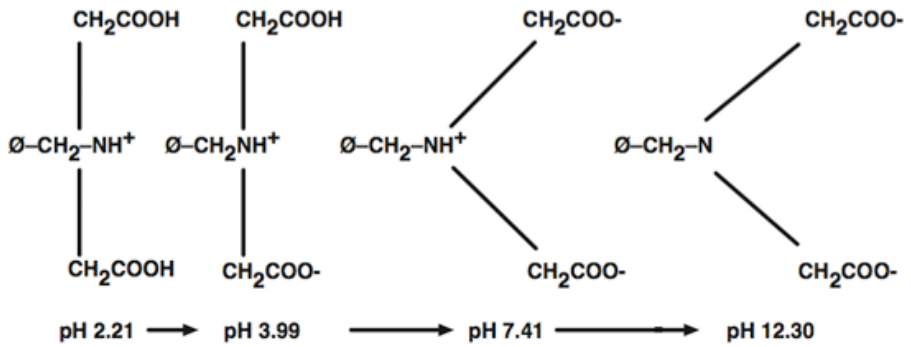

Figure 2.5. Change in structure of Chelex® 100 with increasing pH (figure adapted from Bio-Rad Laboratories [39]).

Chelex® 100 is an ion exchange resin that is more selective for multivalent metals than the standard cation exchange resins, even in highly concentrated salt solution. Average recoveries of REEs, Th, and U are 95 – 98 %. There is one significant disadvantage: Chelation with

Chelex® 100 resin requires the removal of Ca and Mg before eluting of REEs, Th, and U. This makes it inconvenient to work with [4, 16, 38, 39].

Recently, Japanese chemists have started to apply a new resin for preconcentration of REEs and Th in seawater [19, 20]. They use SPE columns packed with NOBIAS-chelate PA-1 chelating resin (Hitachi High-Technologies, Nakaminato, Japan). The retention capacity of NOBIAS-chelate PA-1 resin is pH dependent, as is Chelex® 100. However, it has a better analyte recovery of almost 100 % [19, 20, 40]. NOBIAS-chelate PA-1 resin consists of polyamines and polycarboxyl functional groups immobilized on hydrophilic methacrylates (Figure 2.6) [41].

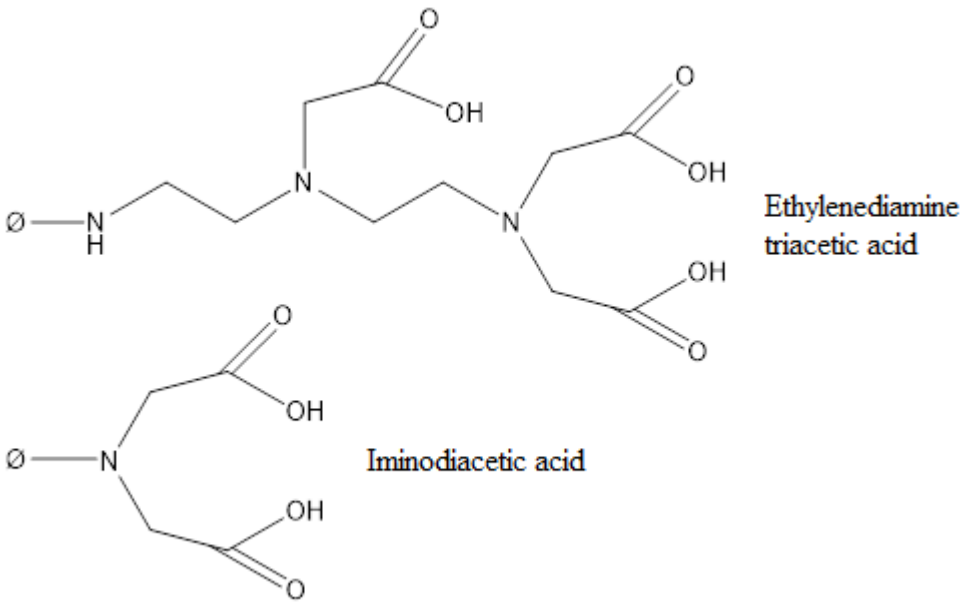

Figure 2.6. NOBIAS-chelate PA-1 chelating resin structure.

2.2. Certified reference materials

"Certified reference material is reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes its traceability to an accurate realisation of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence" [42]. Thus, there are various types of CRMs, including environmental materials with certified property values. However, there is no CRM of seawater with certified concentrations of REEs, Th, and

U. Therefore, purchased artificial seawater, spiked with REEs, Th, and U in-lab, was used for method development in this project.

2.3. ICP-MS principle

ICP-MS is generally considered the first-choice for determination of concentrations of trace and ultra-trace metal ions in aqueous samples [43]. ICP-MS has high sensitivity and low LOD (ng/L range) and can detect many elements at the same time [4, 43]. However, ICP-MS has a low tolerance of about ≤ 0.2 % of total dissolved solids (TDS).

Different ICP-MS designs are available. Their instrumental composition is similar: They have a sample introduction system, ionization source (ICP), mass analyser, detector, and data processing computer (Figure 2.7). The engineering design and implementation of these components can vary significantly.

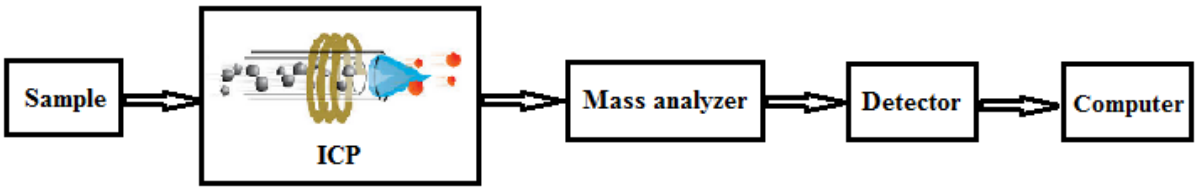

Figure 2.7. Basic instrumental components of an ICP-MS.

A sample is introduced into the instrument in a liquid form by a pump. Analytes ionized in the ICP-stage are directed into a mass analyser through an interface region (metal cones) and ion-focusing system. In the mass analyser, ionized analytes are separated according to mass to charge ratio, before finally reaching the detector, which records the number of electronic pulses counted per second [43].

2.4. ICP-OES principle

ICP-OES tolerates up to 5 % TDS [44], but has a high LOD, i.e., µg/L range [43], and cannot assess concentration of REEs, Th, and U in seawater. However, ICP-OES can be used to determine the necessary dilution of the sample prior to ICP-MS: The sample, if containing

more than 10 % TDS, is diluted step-wise until a measurable level is obtained, and this value is used to calculate the required dilution for ICP-MS analysis, i.e., to achieve TDS ≤ 0.2 %. Figure 2.8 depicts a standard ICP-OES design.

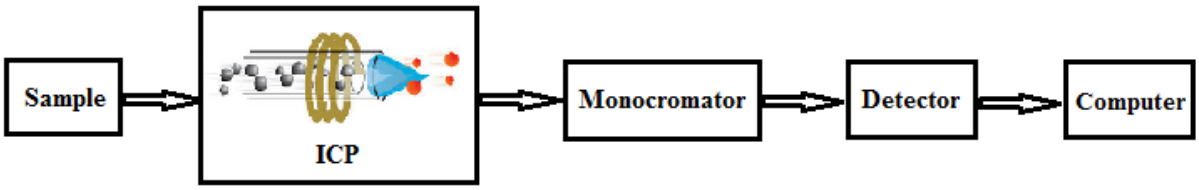

Figure 2.8. Basic instrumental components of an ICP-OES.

Both instruments have the sample introduction- and ICP part in common. However, the plasma in ICP-OES is used to generate photons by excitation of electrons of atoms and ions to a higher energy level. When the electrons "fall" back to ground state, wavelength-specific photons that are characteristic of the element of interest are emitted. These photons are directed to the detector that records radiation intensity [43].

2.5. Limit of detection and limit of quantification

Limit of detection (LOD) is the lowest concentration or quantity of an analyte that can be reliably *detected*, whereas limit of quantification (LOQ) is the lowest concentration or quantity of an analyte that can be reliably *quantified* [45].

Blanks are analysed to determine if they contribute to the measured signal of analytes in a sample, and thus need to be corrected for. STDs of blanks are used to estimate LOD and LOQ. There are two types of blanks that are commonly used, i.e., reagent blank and sample blank: Reagent blank is a reagent used during the analytical process, including solvents used for extraction and dilution. Sample blank is a sample matrix with no analyte present [46]. *Method* LOD and LOQ is calculated based on *sample blank* measurements, where the sample blank is taken through the whole analytical procedure. *Instrument* LOD and LOQ is calculated based on *reagent blank* measurements, where the reagent blank is not taken through the whole analytical procedure, but presented directly to the measuring instrument [46].

3. Experimental

3.1. Instrumentation

ICP-MS instrument (NexION® 300D) purchased from PerkinElmer Inc. (Waltham, MA, USA) was used for determination of REEs, Th, U, and In. The instrument software was NexION® ICP-MS Software (version 1.2), from the same producer. Operating conditions are summarized in Table 6.1. in Appendix.

ICP-OES instrument (Varian Vista AX CCD Simultaneous ICP-AES) purchased from Varian Inc. (Palo Alto, CA, USA) was used for determination of Na, Mg, Ca, and K. The instrument software was Vista PRO ICP-OES CCD Simultaneous (version v4.0 b425), from the same producer. Operating conditions are summarized in Table 6.2, and measured wavelengths are summarized in Table 6.3 in Appendix.

Four-channel peristaltic pump (Minipuls® 3) purchased from Gilson Inc. (Middleton, WI, USA) was used to pass the samples through the SPE-setup at a constant speed. Analytical balance (Sartorius® CP224S) purchased from Sartorius AG (Göttingen, Germany) and pH-meter (Orion™ 420A+) purchased from Thermo Scientific (Columbia, MD, USA) were used during the project.

Strong cation exchanger (SCX), silica-based Strata® SCX packed tubes of 70 Å (500 mg) with carbon load 9 %, and empty polypropylene 60 mL SPE tubes and frits for 60 mL SPE tubes were purchased from Phenomenex Inc. (Torrance, CA, USA).

Glass volumetric flasks used in the project were all of class A and had following volumes and producers: 100 mL, 200 mL, and 500 mL, VWR International (Radnor, PA, USA), 50 mL, BRAND GMBH + CO KG (Wertheim, Germany), and 250 mL, Belden Inc. (St. Louis, MO, USA). Polypropylene bottles of 50 mL, 250 mL, and 500 mL, purchased from Fisher Scientific AS (Hampton, NH, USA), were used for sample collecting and storage. Sterile polypropylene tubes of 15 mL (120 × 17 mm) and 50 mL (115 × 28 mm), purchased from Sarstedt AG & Co (Nümbrecht, Germany), were used to collect SPE eluates, and as solution vessels during ICP-MS and ICP-OES procedures.

3.2. Chemicals and samples

Chelex® 100 resin of 50 – 100 mesh with chelating capacity of 0.6 meq/g was purchased from Sigma-Aldrich Co. LLC (St. Louis, MO, USA).

Multielement standard solution of REEs and Th (100 µg/mL), and single element standard solutions of U (1000 µg/mL) and indium (In) (1000 µg/mL) for atomic spectroscopy, were purchased from Teknolab AS (Ski, Norway). Multielement standard solutions of Na and K, and Mg and Ca (10 000 µg/mL each metal), and single element standard solutions of Na, Mg, Ca, and K (10 000 µg/mL each metal) for atomic spectroscopy were purchased from Spectrapure Standards AS (Oslo, Norway). Hereafter, purchased standard solutions are termed "stock solutions". Preparation of standard solutions for calibration and spiking (hereafter "prepared solutions") is described in Table 6.4 in Appendix.

Hydrofluoric acid 40 % (m/v), p.a., was purchased from Riedel-de Haën (Seelze, Germany). Ammonia solution 28 % (m/v), p.a., was purchased from VWR International (Radnor, PA, USA). Acetic acid 100 %, p.a., nitric acid 65 % (m/v), Suprapur®, and sodium hydroxide, p.a., were purchased from Merck KGaA (Darmstadt, Germany). Water type 1 (18.2 MΩcm), from Milli-Q® Integral Water Purification System produced by Merck Millipore (Darmstadt, Germany), was used during the project.

Artificial seawater (20 L) was purchased from VWR International LLC (Radnor, PA, USA). The concentrations of the main seawater elements, as displayed on the label, are presented in Table 3.1. The content of the purchased artificial seawater was controlled by ICP-OES.

Table 3.1. Content of the artificial seawater by VWR.

Salt, formula	Concentration, g/L
NaCl	26.5
$MgCl_2$	2.4
$MgSO_4 \times 7H_2O$	6.75
$CaCl_2 \times 2H_2O$	1.46
KCl	0.73
Na_2CO_3	0.2
NaBr	0.28

Environmental samples of 500 mL seawater were collected in Fuengirola, Málaga, Spain (36°31'52"N 4°37'26"W) 26.03.2017, and Oslo, Norway (59°54'35"N 10°42'25"E) 27.03.2017.

3.3. SPE setup

The structure of SPE setup is shown in Figure 3.1. The SPE setup included four components, i.e., empty 60 mL polypropylene SPE tube, two frits for 60 mL SPE tubes and Chelex® 100 resin of 50 – 100 mesh.

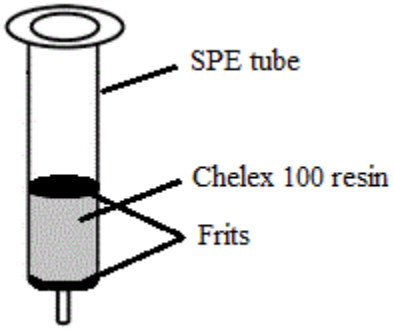

Figure 3.1. SPE setup.

The first frit was placed into the SPE tube. After that, a slurry consisting of 5.00 g of Chelex® 100 resin and 10.0 mL water type 1 was transferred into the SPE tube. Most of the water was removed at 1.0 mL/min pumping speed. The water type 1 was used to wet the second frit prior to its placing on the top of the Chelex® 100. Wetting the frit prevents flipping during forced descent in the tube, and thus protects the flat surface of the resin. Hereafter, a packed SPE tube is termed “SPE column”. Figure 3.2 shows both loaded SPE tube with the slurry and ready-to-use SPE column.

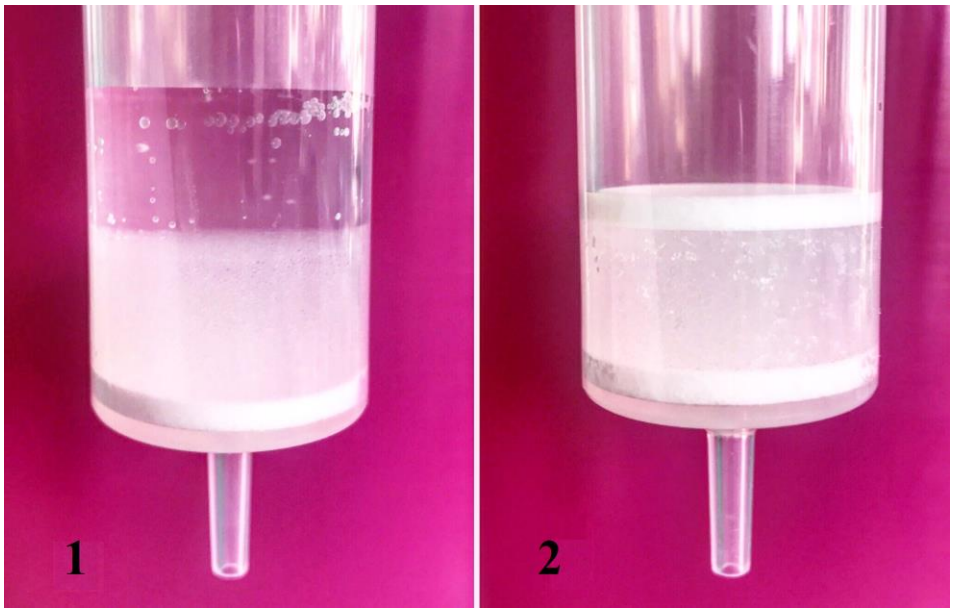

Figure 3.2. 1) Loaded SPE tube with slurry of Chelex® 100 resin 2) Ready-to-use SPE column.

3.4. Regeneration of the SPE columns

After each SPE session the columns were regenerated to sodium form. The first step was rinsing: 10.0 mL 2 M HNO_3 was applied at 1.0 mL/min pumping speed followed by 50 mL of water type 1 at the speed of 1.5 mL/min. The second step was converting the resin into a salt form: 10.0 mL 1 M NaOH was applied at 1.0 mL/min pumping speed followed by 50 mL of water type 1 at the speed of 1.5 mL/min.

3.5. Preparation of ICP-MS for determination of trace elements

Determination of trace elements by ICP-MS requires high purity of the instrument to avoid cross contamination. To obtain proper rinsing, it is necessary to follow further steps after switching on the instrument: 3 min rinsing with 8.4 % (m/v) HF, 5 min rinsing with water type 1, 10 min rinsing with 1 M HNO_3, and 15 min rinsing with 0.5 M HNO_3.

3.6. Calibration solutions for ICP-OES and ICP-MS sample analyses

All calibration solutions in were prepared with 0.5 M HNO_3. Sample defined as blank was pure 0.5 M HNO_3.

Two series of four calibration solutions each were prepared prior to ICP-OES measurements: Containing either Na, Mg, Ca, and K, or only K. The concentrations of each metal in the solutions were: 0 µg/mL, 12.5 µg/mL, 25 µg/mL and 50 µg/mL. For detailed information on preparation of calibration solutions, see Tables 6.5 and 6.6 in Appendix.

The ICP-MS instrument allows for various settings when creating a calibration curve, i.e., weighted regression, linear through zero, or simple linear regression. Simple linear regression was chosen. Three series of multielement calibration solutions, containing REEs, Th, and U were prepared prior to ICP-MS. The series had the following concentrations of each metal: 0 ng/L, 50 ng/L, 100 ng/L, and 200 ng/L; 0 µg/L, 1.25 µg/L, 2.50 µg/L, and 5.00 µg/L; and 0 µg/L, 500 µg/L, 1000 µg/L, and 2000 µg/L. Different series of calibration solutions were used according to the concentration of analytes in a sample. For analyses of REEs, Th, and U containing In as IS, stock solution of REEs and Th, and stock solutions of U and In were utilized. Calibration solutions containing IS had equal concentration of In and REEs, Th, and U: The concentrations of each metal were the following: 0 µg/L, 1.25 µg/L, 2.50 µg/L and 5.00 µg/L. For detailed information on preparation of calibration solutions, see Tables 6.7 – 6.10 in Appendix.

3.7. Limit of detection and limit of quantification for ICP-MS

Data for determination of instrument LOD and LOQ for ICP-MS were obtained by two different approaches. In the first method, ten blank samples were measured and standard deviation (STD) calculated. In the second method, random calibration solutions were measured in between each blank measurement, to a total of four blank measurements, and STD was calculated. LOD was calculated as 3 times STD, LOQ as 10 times STD. Five different calibration solutions of REEs, Th, and U were prepared at concentrations 0 ng/L, 25 ng/L, 50 ng/L, 75 ng/L, and 100 ng/L, respectively. Sample defined as blank was pure 0.5 M

HNO_3. All measurements were performed the same day. For detailed information on preparation of calibration solutions, see Table 6.11 in Appendix.

3.8. Procedures for optimization of SPE and ICP-MS procedures

3.8.1. Analysis of simulated seawater using strong cation exchanger

Four simulated seawater samples spiked with REEs and Th were prepared. Stock solution of REEs and Th, and stock solutions of Na, Mg, and Ca were used. First, 22.00 mL Na-, 6.50 mL Mg-, and 2.00 mL Ca-solutions were placed in 50 mL volumetric flasks, to create samples containing 0.22 g Na, 0.065 g Mg, and 0.02 g Ca. Subsequently, 1.00 mL of multielement stock solution of REEs and Th was added. Finally, to the four flasks it was added 0 mL, 0.90 mL, 2.60 mL, and 4.35 mL, respectively, of 65 % (m/v) HNO_3, to obtain 0.25 M, 0.50 M, 1.00 M, and 1.50 M acid contents in the finished 50 mL samples. Water type 1 was added to the volumetric flasks until the mark.

Four Strata® SCX columns were utilized, i.e., one column for each sample. After wetting SPE column with 10.0 mL water type 1, 10.00 mL of each sample was applied. 10.00 mL 5 M HNO_3 was applied during the final elution step. Four final eluates were collected, diluted 100 times with 0.5 M HNO_3 and the concentrations of Na, Mg, and Ca were measured with the help of ICP-OES. The trial was terminated prior to determination of the concentrations of REEs and Th.

3.8.2. SPE of REEs, Th, and U from spiked artificial seawater at sample pH 5.0, 6.0, 7.0, and 8.0

Four samples of 200 mL artificial seawater were spiked with both 1200 µL stock solution of REEs and Th, and 400 µL prepared solution of U (250 µg/mL). This provided a final concentration of REEs and Th of 594.3 ± 0.2 µg/L (mean ± STD) of each metal, and a final concentration of U of 495.2 ± 0.2 µg/L. The four spiked samples were adjusted with ammonia and acetic acid solutions to four different pH values; 5.0, 6.0, 7.0, and 8.0. Four 50 mL

conditioning solutions with pH 5.0, 6.0, 7.0, and 8.0, respectively, were prepared by adding drops of ammonia and acetic acid solutions to 50 mL water type 1 until the needed pH was achieved. Furthermore, 0.05 M ammonia acetate solution with pH 6.0 was prepared for the buffer-washing step in the SPE procedure (for detailed information on preparation of the buffer solutions, see Table 6.12 in Appendix). Four SPE columns, packed with Chelex® 100, were used in parallel in the experiment since a four-channel pump was used. The sample with pH 5.0 was evenly distributed among the four SPE columns. Further, the same four columns were utilized for the sample with pH 6.0, then pH 7.0, and finally pH 8.0. The SPE procedure for this experiment is displayed in Table 3.2.

Table 3.2. SPE procedure of REEs, Th, and U from spiked artificial seawater at sample pH 5.0, 6.0, 7.0, and 8.0.

Step	Applied solution	Pumping speed, mL/min
Prewashing	10.0 mL 2 M HNO_3	1.0
	50 mL water type 1	1.5
Conditioning	50 mL conditioning solution	1.5
Loading	50.5 ± 0.1 mL replicate	1.0
Buffer-washing	10.00 mL buffer pH 6.0	1.0
Final elution	10.00 mL 2 M HNO_3	1.0

The eluates from each step were collected. The loading and buffer-washing step eluates were diluted 100 times and the final elution step eluate was diluted 10 times. All the dilutions were made with 0.5 M HNO_3. The concentration of Na, Mg, Ca, and K was determined by ICP-OES. The concentration of REEs, Th, and U was measured in 10 times diluted eluate sample by ICP-MS. After that, aliquots of the already 10 times diluted solutions were diluted an additional 2 times, and the concentration of REEs, Th, and U was determined again.

3.8.3. SPE of REEs, Th, and U from spiked water type 1 at sample pH 4.0, 5.0, 6.0, 7.0

Four samples of 200 mL water type 1 were spiked each with both 1200 µL stock solution of REEs and Th, and 400 µL prepared solution of U (250 µg/mL). This provided a final

concentration of REEs and Th of 594.3 ± 0.2 µg/L of each metal, and a final concentration of U of 495.2 ± 0.2 µg/L. The spiked samples were adjusted with ammonia and acetic acid solutions to pH 4.0, 5.0, 6.0, and 7.0, respectively. Four new SPE columns were employed. The conditioning and buffer solutions were not used during this SPE procedure, whereas the other steps were the same. The concentration of REEs, Th, and U was measured in 2 times diluted final eluates by ICP-MS. Water type 1 was used for dilution.

3.8.4. Elution profile of REEs, Th, and U in Spiked water type 1 (µg/L range), 2 M HNO_3

200 mL water type 1 was spiked with both 1200 µL stock solution of REEs and Th, and 400 µL prepared solution of U (250 µg/mL). This provided a final concentration of REEs and Th of 594.3 ± 0.2 µg/L of each metal, and a final concentration of U of 495.2 ± 0.2 µg/L. The spiked sample was adjusted with ammonia and acetic acid solutions to pH 5.0. SPE columns were prewashed with 10.0 mL 0.5 M HNO_3 at 1.0 mL/min speed followed by 50 mL of water type 1 at 1.5 mL/min speed. The sample was evenly distributed among the four SPE columns. The pumping speed was 1.0 mL/min under the loading step. To create an elution profile, 16.00 mL of 2 M HNO_3 was applied to each column in increments of 2.00 mL. Eight final eluates from each column, i.e., a total of 32 final eluates, were collected and diluted 4 times with water type 1. The concentration of REEs, Th, and U was determined by ICP-MS.

3.8.5. Elution profile of REEs, Th, and U in spiked water type 1 (ng/L range), 2 M HNO_3

The previous trial was repeated except for changing a spiking amount of REEs, Th, and U: 200 mL water type 1 was spiked with both 200 µL prepared solution of REEs and Th (100 µg/L of each metal), and 200 µL prepared solution of U (100 µg/L). This provided a final concentration of REEs, Th, and U of 99.6 ± 0.1 ng/L of each metal. Four unused SPE columns were used. The 32 final eluates were collected and diluted 2 times with water type 1 prior to ICP-MS measurements.

3.8.6. Elution profile of REEs, Th, and U in spiked water type 1 (ng/L range), 3 M HNO_3

The previous trial was conducted one more time after replacing 2 M HNO_3 with 3 M HNO_3. The collected eluates were diluted 2 times with water type 1 prior to ICP-MS measurements. Then, already diluted eluates were diluted an additional 2 times and concentration of REEs, Th, and U was determined again.

3.9. Analyses of samples with different content of matrix cations: Mixing of water type 1 and artificial seawater in different ratios

Four series of 50.0 mL samples (four in each series) had the following content: 0 mL artificial seawater and 50.0 mL water type 1, 10.0 mL artificial seawater and 40.0 mL water type 1, 25.0 mL artificial seawater and 25.0 mL water type 1, 50.0 mL seawater and 0 mL water type 1. Each sample was spiked with both 1.00 mL prepared solution of REEs and Th, and 1.00 mL prepared solution of U. The spiked samples contained 100 µg/L of each metal. The final concentration of REEs, Th, and U was 1.91 ± 0.01 µg/L of each metal. All samples were adjusted to pH 5.0 with ammonia and acetic acid solution. All samples were loaded on the columns at pumping speed of 1.0 mL/min, which was the same for the following SPE steps. 10.00 mL of 0.05 M ammonia acetate buffer with pH 5.00 was used in the buffer-washing step for the samples containing seawater. 10.00 mL 2 M HNO_3 followed by 5.00 mL 3 M HNO_3 were used in the final elution step. The aliquots of all the eluates were diluted 20 and 10 times. The aliquotes of the final eluates derived from the samples, containing 0 mL and 10.0 mL artificial seawater, were additionally diluted 5 times. The concentration of REEs, Th, and U was determined by ICP-MS in the diluted aliquots. All dilutions were made with 0.5 M HNO_3.

3.10. Application of the developed method on environmental samples

Two replicates of 50.0 mL were taken from each environmental seawater sample of 250 mL, collected in Fuengirola, Spain, and Oslo, Norway. Two 50.0 mL artificial seawater samples

were both spiked with 1.00 mL prepared solution of REEs and Th, and 1.00 mL prepared solution of U. The solutions contained 100 µg/L of each metal. The spiked samples contained 100 µg/L of each metal. The final concentration of REEs, Th, and U was 1.91 ± 0.01 µg/L of each metal. In addition, two *unspiked* 50.0 mL artificial seawater samples were included in the experiment. The replicates from the environmental samples, and the spiked and unspiked artificial seawater samples, were all adjusted to pH 5.0. Two identical series of SPE procedures were conducted. Four unused SPE columns were used. Except for using 2 M HNO_3 for the last 5.00 mL of the final elution step, the SPE procedure was the same as when imitating environmental samples. All the eluates were collected for further analysis by ICP-MS. The whole SPE procedure was repeated with the second series of solutions after regenerating the columns.

During this experiment, In was used as IS. Prior to the addition of In, 200 µL aliquots were taken from the final eluates. They were diluted 20 times, and concentration of REEs, Th, U, and In was determined. Then, 100 µL of prepared solution of In (500 µg/L) was added to the remaining contents of each of the final eluates. After that, 200 µL-, 400 µL-, 1.00 mL-, and 2.00 mL aliquots from the final eluates containing IS were diluted 20-, 10-, 5-, and 2 times, respectively, to reach LOQ of REEs, Th, and U, in all analysed solutions, by ICP-MS. All the dilutions were made with 0.5 M HNO_3.

4. Results and discussions

4.1. Opening remarks

In this thesis, results and discussions are combined, because most of the work is in fact method development. Hence, most of the data was obtained during stages of procedure establishment. This chapter, therefore, presents chronological steps of the method development process, its drawbacks and obstacles, ideas behind choices and actions, data from each step and its interpretation. Finally, results from actual environmental samples, obtained by the proposed method, conclude this work.

4.2. Simulated seawater versus purchased artificial seawater

In the initial stages of optimizing the SPE procedure, simulated seawater was prepared from *stock solutions*. These solutions are costly, which made it highly expensive to prepare simulated seawater for each trial. In addition, all the stock solutions are prepared with 2.5 % (m/v) HNO_3, whereas real seawater hardly contains NO_3^- [47]. Simulated seawater was used only in SCX trials. Commercially available artificial seawater has a closer resemblance to actual seawater, and is also considerably cheaper than the homemade alternative. For these reasons, artificial seawater was purchased rather than prepared for the remainder of this study. Artificial seawater with a known content was supplied from VWR international in a 20 L container. This assured a constant matrix content for all samples during the method development. The concentration of the main cations in the purchased artificial seawater was controlled with the help of ICP-OES. Table 4.1 shows some difference between the concentrations obtained from ICP-OES analysis and the concentrations calculated from the stated salt amounts on the label of the artificial seawater container.

Table 4.1. Metal concentration in artificial seawater by ICP-OES results and by VWR.

Element	Ca	Mg	Na	K
Concentration ICP-OES, g/L	0.6	1.51	10.8	0.8
Concentration VWR, g/L	0.4	1.47	10.6	0.4

The largest difference between measured and stated concentration is found for K. Calibration solutions should if possible mimic sample solutions, hence multielement calibration solutions were initially applied. However, calibration curve for K could not be obtained after several attempts using multielement calibration solutions containing Na, Mg, Ca, and K. Calibration solutions utilizing only K standard solution was therefore prepared, which solved the issue. Thus, calibration curves for Na, Mg, and Ca were obtained by multielement solutions, whereas K was analysed using single element calibration solutions. In this ICP-OES analysis concentration of K was determined by measuring atomic emission. This means that for a given solution, ICP-OES signal strength depends on the degree of transition from atomic to ionized form of an element. In a multielement solution, the mere number of metals will suppress this transition for any single element. As a result, there is more K in atomic form in a sample compared to the calibration solutions. This explains why the measured value for K is substantially higher than that provided by VWR. The objective of further experiments was to assess degree of elution during SPE. A consistent discrepancy between measured and VWR-stated concentrations of elements does then not influence the results, since it is the relative concentrations that are of interest and not the absolute amounts of Na, Mg, Ca, and K.

4.3. Challenges with contamination of the ICP-MS system and other equipment

When working at ng/L range, a procedure to adequately rinse the ICP-MS setup is crucial for successful experiments, as it hinders contaminations in samples and calibration solutions. Ensuring adequate levels of cleanliness posed a major challenge, and several initial trials failed because of contaminations. The in-lab established routine for rinsing of the ICP-MS was not sufficient for the experiments performed in this study. When other users run samples containing REEs, Th, or U at higher concentration, the risk of cross contamination is almost absolute, and an effective rinsing procedure must be applied. Consequently, a specialized rinsing procedure had to be developed for this study. This 30-min procedure is described in chapter 3.5. Adequate cleanliness of equipment such as plastic containers, test tubes, and pump tubes could only be obtained through exhaustive and rigorous rinsing procedures, not readily applied to daily trials. Thus, this equipment needed to be disposable and brand new for each trial, to sufficiently minimize contamination risk and to streamline lab-work. Some

researchers who work with trace metals determination conduct their experiments in a cleanroom [14], i.e., a room with controlled level of contamination, which is specified as an allowed number of particles within a certain size-range, per volume [43]. When working specifically with REEs, Th, and U, however, this is not necessary as these metals are unlikely to be found in the laboratory air. REEs, Th, and U are in general unusual indoor contaminants.

4.4. Challenges with ng/L range calibration curve

Calibration solutions with metal concentrations 0 ng/L (pure 0.5 M HNO_3), 25 ng/L, 50 ng/L, and 100 ng/L were prepared prior to LOD(LOQ)i investigation. However, to create a calibration curve in the ng/L range is challenging. When each solution was prepared directly from *prepared solutions* of REEs and Th, and U (25 µg/L each), a linear calibration curve could not be obtained. One possible reason is that the *prepared solutions* were made by diluting the stock solutions of REEs and Th in three steps, and U in four steps. Furthermore, the best-suited micropipette available was 100 µL, and this micropipette was used to prepare all calibration solutions. For example, to draw 400 µL of a stock solution, four times 100 µL were drawn. The error of the final volume would thus be the pipette´s systematic error multiplied by four, which is larger than the error of a 400 µL micropipette. Hence, another approach was applied. First, the 100 ng/L calibration solution was prepared, then an aliquot of this solution was diluted twice to prepare the 50 ng/L calibration solution. Subsequently, an aliquot of the 50 ng/L solution was again diluted twice to make the 25 ng/L calibration solution. Through this procedure, a linear calibration curve was finally obtained.

4.5. Limit of detection and limit of quantification of REEs, Th, and U for ICP-MS

The concentrations of REEs, Th, and U in ICP-MS analysed solutions are close to LOD and LOQ. Therefore, their determination becomes imperative. Since a sample blank (seawater without analytes) was unavailable, a reagent blank (0.5 M HNO_3) was used to determine instrument LOD and LOQ, ($LOD(LOQ)_i$). It is feasible to extrapolate method LOD and LOQ, ($LOD(LOQ)_m$), as a multiple of $LOD(LOQ)_i$ and the net concentration- or dilution factor of

the analytes. For example, if a sample is preconcentrated five times through SPE and then diluted two times prior to ICP-MS, $LOD(LOQ)_m$ will be $LOD(LOQ)_i$ times 0.4.

However, solutions analysed by ICP-MS can potentially influence measured concentrations in consecutive solutions to be measured. One way to assess this possible error source, is by measuring analyte-containing solutions in between blanks.

$LOD(LOQ)_i$ for ICP-MS was therefore determined by two different approaches; using only blank samples, or also including random calibration solutions between each blank (see chapter 3.7. for details).

The mean $LOD(LOQ)_i$ was used for preparation of spiked solutions and diluted eluates in further experiments. The mean concentration of REEs, Th, and U in each approach and the mean $LOD(LOQ)_i$ are shown in Table 4.2. Detailed data are shown in Tables 6.13 – 6.15 in Appendix. The table shows the specific isotopes measured by ICP-MS, chosen for their abundance in nature.

Table 4.2. Mean concentration of REEs, Th, and U in each approach, and mean $LOD(LOQ)_i$ of REEs, Th, and U for ICP-MS for the two approaches.

Analyte	1st Approach mean concentration, ng/L	2nd Approach mean concentration, ng/L	Mean LOD, ng/L	Mean LOQ, ng/L
^{45}Sc	21	22	11	38
^{89}Y	4.3	4.6	0.5	1.6
^{139}La	4.06	4.11	0.31	1.02
^{140}Ce	2.8	3.0	0.4	1.0
^{141}Pr	1.09	1.08	0.22	0.74
^{142}Nd	0.1	0.1	1.0	3.3
^{152}Sm	1.0	1.2	3.3	11.1
^{153}Eu	-2.3	-2.2	1.4	4.6
^{158}Gd	0.8	0.8	0.9	3.0
^{159}Tb	3.415	3.418	0.017	0.055
^{164}Dy	2.1	2.1	0.6	1.9
^{165}Ho	4.43	4.45	0.08	0.26
^{166}Er	2.3	2.4	0.3	1.1
^{169}Tm	-1.35	-1.36	0.07	0.23
^{174}Yb	-0.4	-0.3	0.4	1.4
^{175}Lu	1,86	1,89	0.15	0.51
^{232}Th	4	6	3	9
^{238}U	6.7	7.0	0.8	2.6

For most of the metals there were some variations in measured concentrations between the two approaches, the second resulting in marginally higher measured concentrations as expected. This demonstrates some degree of influence of already analysed solutions on consecutive measurements. However, this influence was so minute that it was not considered a relevant error source. The mean concentration values of REEs, Th, and U in the blank calculated from the two methods, was subtracted from the obtained results in the following experiments.

4.6. Choice of sorbent

The sorbent best suited to the planned experiments was NOBIAS-chelate PA-1 chelating resin. However, the NOBIAS-chelate PA-1 resin was only possible to purchase in bulk, in quantities of 150 g, at the price of 40 000 NOK, and with a delivery time of three months. This made it unfeasibly expensive, and the delivery time was incompatible with the project. Therefore, Chelex® 100, the second-best option, was considered. Chelex® 100 was also only available in bulk, but could be purchased in quantities of 100 g, at the price of 2100 NOK, and with a delivery time of one and a half week. Consequently, Chelex® 100 was chosen as sorbent. Awaiting delivery of Chelex® 100, Strata® SCX, a sorbent already available in the laboratory, was used. Strata® SCX is a silica based sorbent containing benzene sulfonic acid groups, well suited to adsorb weak basic compounds. Simulated seawater spiked with REEs, Th and U was analysed in SCX trials. Unfortunately, the final eluates contained 55 – 80 % of the initial amount of matrix metals (for more details, see Table 6.16 in Appendix). This exceeds the TDS level tolerated by the ICP-MS instrument to such an extent that necessary dilution would render levels of analytes undetectable. The trials with SCX were therefore terminated, and further experiments were postponed until the imminent arrival of Chelex® 100.

4.7. Maintenance of the SPE columns

Chelex® 100 is a resin supplied in sodium form. In this study, Chelex® 100 was utilized in hydrogen form to reduce the quantity of sodium in the final eluate. For this reason, every SPE procedure started with application of 10.0 mL 2 M HNO_3 to the column to replace Na^+ with

H^+. However, according to the supplier [39], if the resin is left in hydrogen form for hours its chelating capacity decreases. As each SPE procedure (four SPE columns in parallel) took approximately three hours, decrease in the chelating capacity was expected.

Chelex® 100 shrinks to about half of the initial volume when going from sodium to hydrogen form (Figure 4.1).

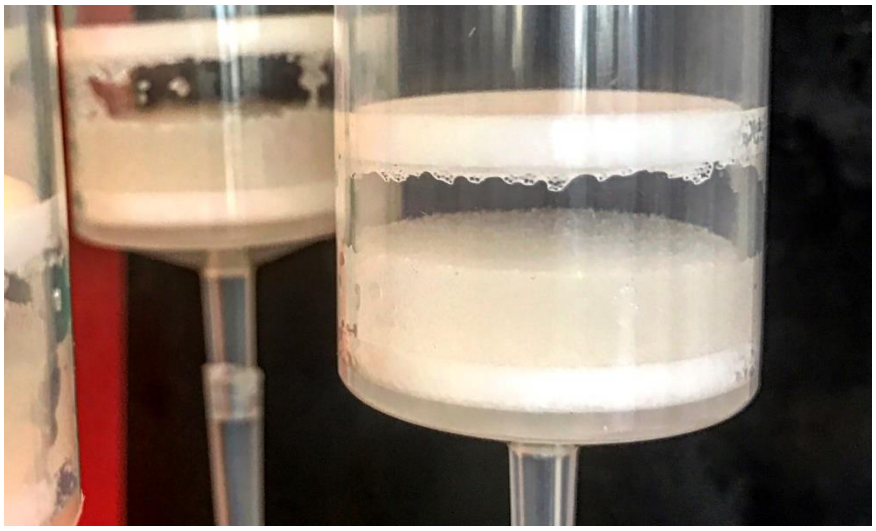

Figure 4.1. Chelex® 100 in hydrogen form.

After each SPE procedure, Chelex® 100 must be regenerated to sodium form, which is done by 1 M NaOH solution. After regeneration, the resin is expected to swell to the initial volume. However, after ten SPE procedures (about 30 hr of use) the Chelex® 100 ceased to visibly swell. This implies detrimental decrease in its chelating ability from being in the hydrogen form for approximately three continuous hours. Therefore, it became necessary to adjust the procedure to reduce the time the resin was in the hydrogen form. For this reason, the conditioning SPE step was sacrificed as it took almost 30 min. Further experiments showed that this did not influence retention of analyte. One possible explanation for this is that the sample volume was relatively high, 50 mL, and the analyte concentration comparably low, ng/L range. Thus, the sample could condition the resin by itself without any notable loss of analyte. This change was favourable not only in terms of resin integrity, but it also reduced the experimental procedure time by 30 min.

4.8. SPE preconcentration as a step, not the net effect of manipulations prior to ICP-MS

Through the SPE procedure, matrix elements are removed and analytes concentrated. This process is termed preconcentration, indicating a concentration of analytes prior to ICP-MS. However, as long as analytes remain above LOQ, dilution to further decrease concentration of matrix elements may be beneficial to analysis. Therefore, the net effect of the procedures conducted before ICP-MS can in fact be a dilution of analytes: The prime objective is not to concentrate analytes per se, but to arrive at a solution with TDS below ICP-MS tolerance, and analyte concentration above LOQ. In other words, preconcentration is a reference to the SPE step, not the net effect of manipulations prior to ICP-MS.

4.9. Spectral interferences

The measured isotopes were chosen for their abundance in nature. When determining concentration of analytes by ICP-MS, there is always a possibility for interferences. If oxides of analyte- or matrix metals have the same nominal mass as an analyte isotope, its signal is enhanced. This is an example of spectral interference. Potential interferences could occur for some REEs: ^{152}Sm (^{136}Ba^{16}O), ^{153}Eu (^{137}Ba^{16}O), ^{158}Gd (^{142}Nd^{16}O), ^{159}Tb (^{143}Nd^{16}O), ^{165}Ho (^{149}Sm^{16}O), ^{169}Tm (^{153}Eu^{16}O), and ^{174}Yb (^{158}Gd^{16}O) [48]. Ideally, isotopes without potential interferences should be chosen for ICP-MS measurements. However, Tb, Ho, and Tm are monoisotopic, and Eu, Gd, and Yb have no interference-free isotopes. Nevertheless, the interfering oxides are all formed from REEs, the concentrations of the different REEs are all of trace amounts, and the degree of oxide-formation is normally less than 2.5 %. Hence, possible interference caused by oxides is negligible.

Barium (Ba), a seawater matrix component, can cause spectral interferences. However, SPE removal of matrix components renders influence on ICP-MS unlikely. Nevertheless, to rule out this possible source of error, the contribution of Ba oxides to the analyte signal was further investigated. ^{136}Ba^{16}O can interfere with ^{152}Sm signal and ^{137}Ba^{16}O with ^{153}Eu signal. Sm, as opposed to Eu, has interference-free isotopes. Therefore, concentration of ^{152}Sm was measured in parallel with interference-free ^{149}Sm to assess presence of ^{136}Ba^{16}O and, hence,

presence of $^{137}Ba^{16}O$. The determined concentrations of ^{152}Sm and ^{149}Sm were in effect equal. This means that $^{137}Ba^{16}O$ impact on ^{153}Eu signal is negligible.

If oxide spectral interferences had been detrimental, application of a collision cell could be considered. Collision cells are devices utilized in conjunction with ICP-MS to remove interfering polyatomic ions by their collision with a non-reactive gas, e.g. helium (He) [43].

No known oxides have the same nominal mass as the analytes Th and U.

4.10. Search for an optimal sample pH: Spiked artificial seawater

In previous works most comparable to this project, i.e., works in which Chelex® 100 has been used in determination of trace elements in seawater, sample pH of 6.0 was chosen for SPE [15, 16, 49]. However, these studies were all conducted in the same laboratory at Nagoya University, Japan, and Hiroki Haraguchi was the last author of them all. They also employed an on-line SPE system, as opposed to the off-line SPE system used in this project, and their research only comprised determination of some REEs, and U, not Sc and Th. Because of these differences, lack of information on why they chose exactly pH 6.0, and the fact that all the work sprung from the same research group, an independent evaluation of sample pH was performed in this study.

4.10.1. Degree of matrix cations removal at sample pH 5.0, 6.0, 7.0, and 8.0

REEs, Th, and U, and main matrix cations, Na, Mg, Ca, and K, are hard cations, according to the HSAB theory. However, REEs, Th, and U are harder than Na, Mg, Ca, and K [36]. Chelex® 100 is a chelating resin, with ion exchange capability, containing iminodiacetic acid groups that change its ligand properties depending on pH (working range pH 4 – 14) [39]. The inherent challenge is to find the right sample pH to achieve maximum adsorption of REEs, Th and U, and minimum adsorption of Na, Mg, Ca, and K. Iminodiacetic acid is a hard ligand which becomes even harder with lowering of pH. Choosing pH values in the lower end of its working range, 5.0, 6.0, 7.0, and 8.0, for evaluation, should therefore minimize adsorption of Na, Mg, Ca, and K. Therefore, artificial seawater spiked with REEs, Th, and U

was loaded at these pH values during SPE. Eluates from the loading, buffer-washing, and final elution steps were collected. Concentrations of Na, Mg, Ca, and K were determined by ICP-OES, and the eluted part of the metals for each step was calculated. The initial amount of each metal in artificial seawater obtained by ICP-OES was defined as 100 %. Figures 4.2 – 4.4 show the results from the eluates of the loading, buffer-washing, and final elution steps (n – number of analysed replicates). For detailed information on the data, see Tables 6.17 – 6.19 in Appendix.

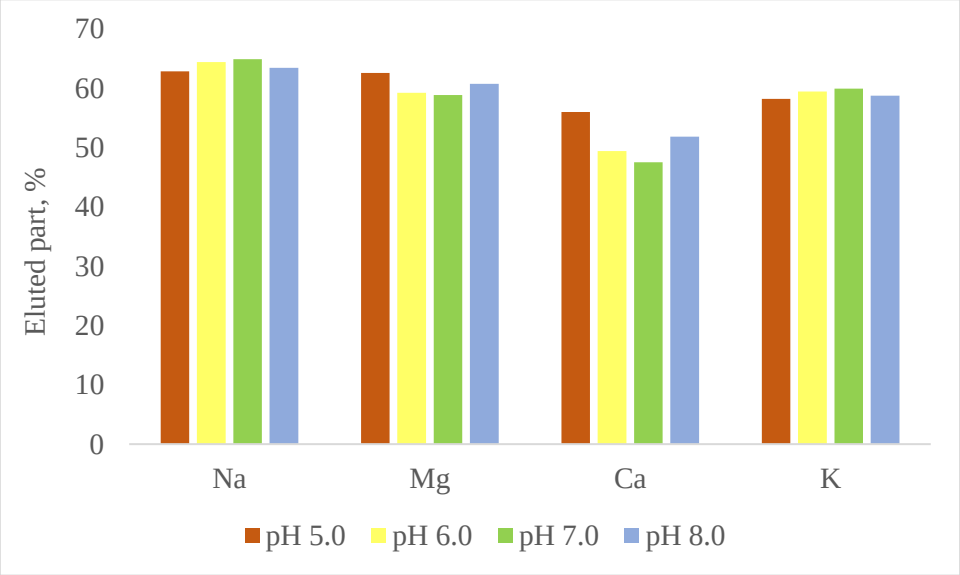

Figure 4.2. Eluted part of Na, Mg, Ca, and K from the loading step at different loading pH conditions (n = 4).

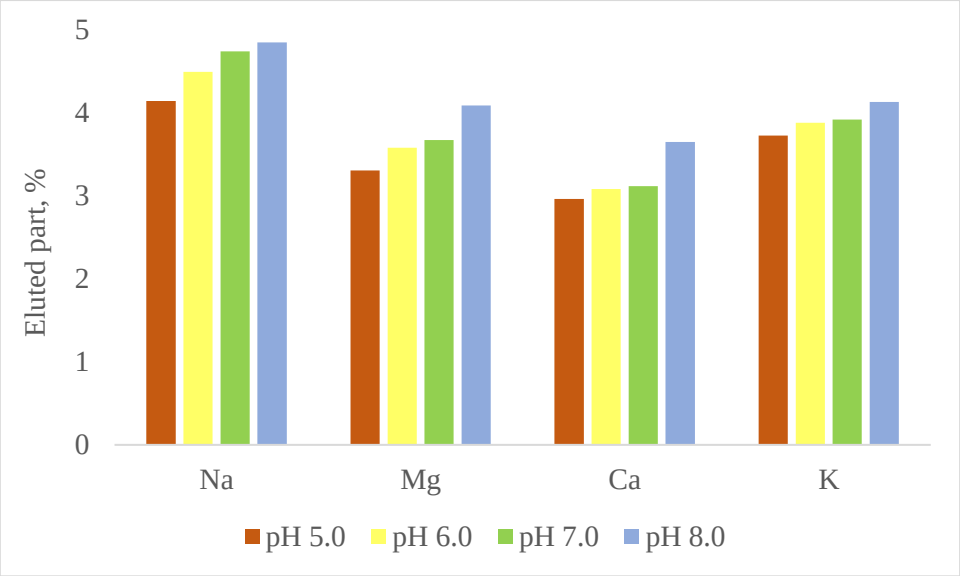

Figure 4.3. Eluted part of Na, Mg, Ca, and K from the buffer-washing step with pH 6.0 buffer at different loading pH conditions (n = 4).

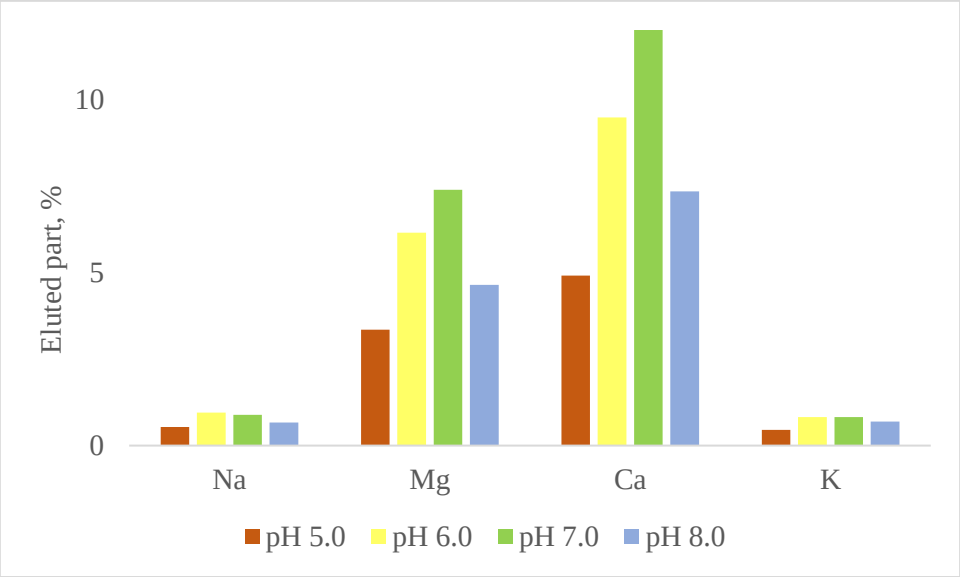

Figure 4.4. Eluted part of Na, Mg, Ca, and K from the final elution step at different loading pH conditions (n = 4).

In the loading step, the divalent cations are most eluted at pH 5.0 and least at pH 7.0, whereas monovalent cations show the opposite tendency. Chelex® 100 thus adsorbs metals with different charges to unequal degrees, without a clear trend, but in a pH-dependent manner. This indicates that ion exchange and chelating properties of the resin change independently of each other when pH changes. The results from buffer-washing and final elution steps support this assumption. In other words, these experiments did not provide a method to reliably predict adsorption and desorption of the analytes and matrix metals at different sample pH through loading, buffer-washing and final elution steps. The main objective of these experiments, however, was to find the pH at which retention of matrix elements was lowest, which in turn would also be the pH at which the final eluate contains less matrix elements. For this parameter, the matrix metals fortunately displayed consistency, and the lowest values for all four metals were obtained at pH 5.0. At this pH value, the calculated concentration of Na, Mg, Ca, and K in the final eluate was 29 ± 1 mg/L, 25.0 ± 0.7 mg/L, 14.3 ± 0.5 mg/L, and 1.8 ± 0.1 mg/L, respectively. That corresponds to 0.53 ± 0.02 %, 3.3 ± 0.1 %, 4.9 ± 0.2 %, and 0.45 ± 0.03 %, respectively, of initial concentration in artificial seawater. The total mass of $NaNO_3$, $Mg(NO_3)_2$, $Ca(NO_3)_2$, and KNO_3 would be 15.7 ± 0.5 mg, which is approximately 0.15 % of total mass of the final eluate. As other dissolved solids are negligible, TDS is lower than 0.2 %, although not greatly so. Therefore, the final eluates should be diluted prior to ICP-MS analysis.

It is unlikely that remaining matrix cations compete with analyte cations for active sites of the resin during SPE: Stability constants of REEs- (except Sc), Th-, and U metal-complexes with iminodiacetic acid vary between 6.78 and 8.93, while for Mg and Ca, stability constants are 2.94 and 2.59, respectively. There is no data about chelating complexes with Na and K [50].

4.10.2. Calculated recovery of REEs, Th, and U at sample pH 5.0, 6.0, 7.0, and 8.0

Artificial seawater was spiked with REEs, Th, and U so that the concentrations in the initial solutions were 594.3 ± 0.2 µg/L of each REE and Th, and 495.2 ± 0.2 µg/L of U. These concentrations are high in comparison to those of real seawater, and were chosen to ensure the detection of all analytes in the method-developing stages of the study. Total quantity of milliequivalents of REEs, Th, and U was 1.2×10^{-2} per loaded replicate, while chelating capacity of the Chelex 100 is 0.6 meq/g. Since amount of resin was 5.00 g per column, 100 % of REEs, Th, and U were expected to be adsorbed.

Aliquots from the final eluates were diluted 10 times prior to ICP-MS determination, because of the high concentrations of the matrix elements and low ICP-MS-tolerance of TDS. The calculated recovery of REEs, Th, and U are presented in Figure 4.5. For detailed information on the data, see Table 6.20 in Appendix.

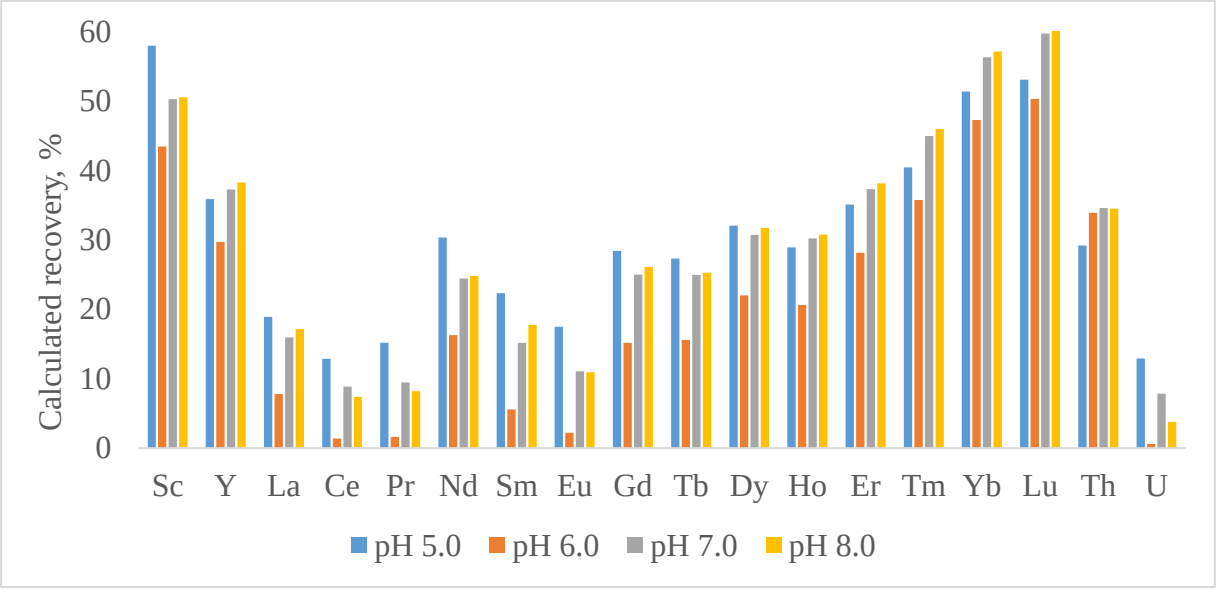

Figure 4.5. Calculated recovery of REEs, Th, and U in the final eluate analysed at 10 times dilution (n = 4).

The calculated recovery varied from 1 to 60 %. This represents both unacceptable variation and degree of recoveries. Comparable results from other publications utilizing Chelex® 100, state consistent recoveries of 85 – 98 % [15, 16].

The poor calculated recovery of the metals was most likely caused by less than optimal experimental conditions. These SPE trials were the last for this set of columns before they became unfit due to unfavourable decrease in chelation capacity of the resin. Degree of chelation by the resin differs between the metals, and for outliers that natively are adsorbed less strongly, a decrease in chelation capacity could render chelation both inconsistent and detrimentally ineffective. This could explain the considerable variations in calculated recovery between metals in these initial trials. Albeit the measured variations in calculated recovery are most likely erroneous, the demonstrated relationship between pH and calculated recovery could possibly be trusted. For all metals, pH 5.0 yielded the highest calculated recovery, which is the same pH value found by ICP-OES to most effectively separate matrix metals from analytes. This, of course, is a major convenience.

However, in addition to being highly diversified, the measured recoveries in this trial were also unsatisfyingly low. One plausible reason for this is that relatively high concentrations of matrix elements negatively influence ICP-MS detection of analytes. To asses if further dilution could improve measured calculated recovery, aliquots diluted 10 times were diluted an additional two times. The calculated recovery of REEs, Th, and U are presented in Figure 4.6. For detailed information on the data, see Table 6.21 in Appendix.

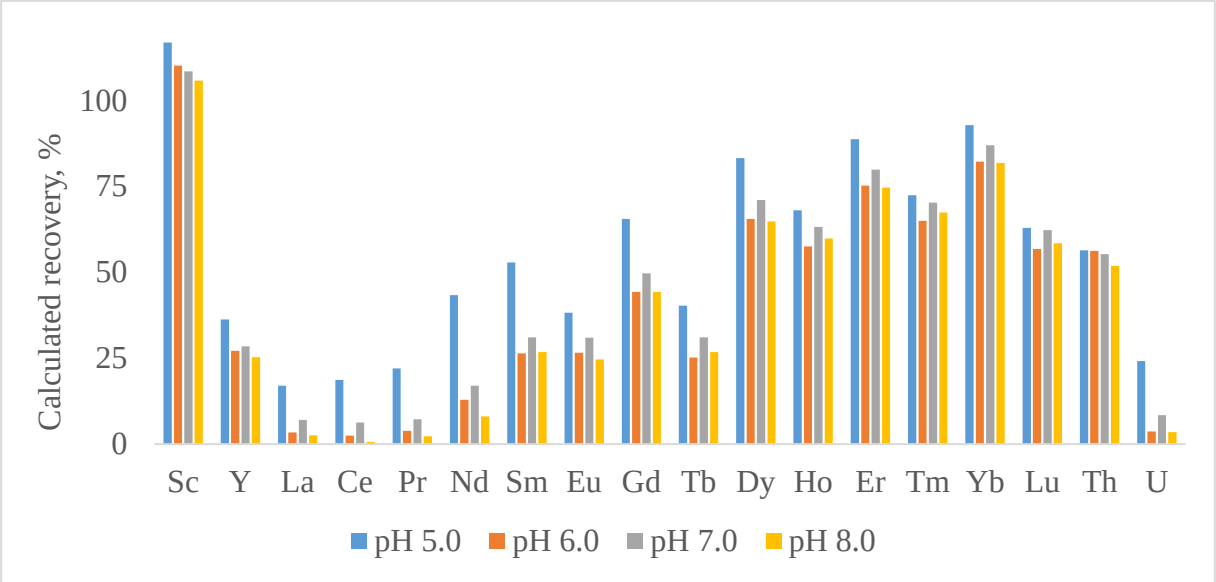

Figure 4.6. The calculated recovery of REEs, Th, and U after SPE in the final eluate analysed at 20 times dilution (n = 4).

When the aliquots from the final eluate are diluted 20 times, the calculated recovery is significantly higher than for 10 times diluted aliquots. This illustrates that higher concentrations of matrix cations indeed probably influence ICP-MS detection of analytes. Naturally, as the aliquots used to make both dilutions are from the same SPE trial, the same variation in calculated recovery between metals is apparent. In addition, for the 20 times dilution, a difference from the 10 times dilution in terms of relationship between sample pH and degree of calculated recovery is revealed. Possible explanations for this are both the presence of impurities in the ICP-MS system from another user, as the dilutions were analysed three days apart, and the effect of oxidation processes. Pr, Nd, Sm, Eu, and Tb form oxides over time, which means that the concentrations of these metals decrease, while the measured concentrations of metals with similar mass as the formed oxides simultaneously increase [48]. Interpretation and predictability of this effect is challenging, due to limited literature on these metals in general. When performing these kinds of experiments, as the first SPE trials showed, it is vitally important to use resins that have persisted in hydrogen form for a limited period. In other words, a finite number of trials can be performed for each column, as the procedure is time consuming and eventually leads to resin deterioration. Furthermore, it is of paramount importance to dilute the 2 M acidic eluates the same day as ICP-MS analysis to minimize risk of oxidation processes, and to analyse all samples in a trial in the same intra-day session to avoid impurities from other users.

4.11. Search for an optimal sample pH: Spiked water type 1

The previous experiment showed calculated recovery of only 1 – 60 %, and other publications present a discrepancy between final eluate and initial analyte concentrations of up to 15 % [15, 16]. This could either be caused by incomplete desorption from resin in the final elution, or loss of analytes during loading and buffer-washing, or a combination of both. To elucidate this, each individual eluate was analysed. In the first eluates of the SPE preconcentration procedure, concentrations of matrix elements are too high to perform ICP-MS. The instrument will be clogged unless the eluates are diluted, but dilution of eluate renders concentrations of analytes below LOD. Therefore, to be able to analyse each individual eluate, spiked water type 1 was utilized instead of artificial seawater. The sample pH range was chosen from 4.0 to 7.0 to assess how the SPE system functioned at pH 4.0, and to re-evaluate functioning at pH 5.0, 6.0, and 7.0. Since the pump had only four channels, pH 8.0 was omitted. The concentration of REEs, Th, and U was the same as in the previous experiment. Unused SPE columns were utilized to avoid cross contamination. For the eluates collected from the loading and buffer-washing step, concentrations of REEs, Th, and U were below LOD. This means that REEs, Th, and U, which were not eluted during the final elution step, was retained in the column. Figure 4.7 shows the calculated recovery of REEs, Th, and U in the final eluate. For detailed information on the data, see Table 6.22 in Appendix.

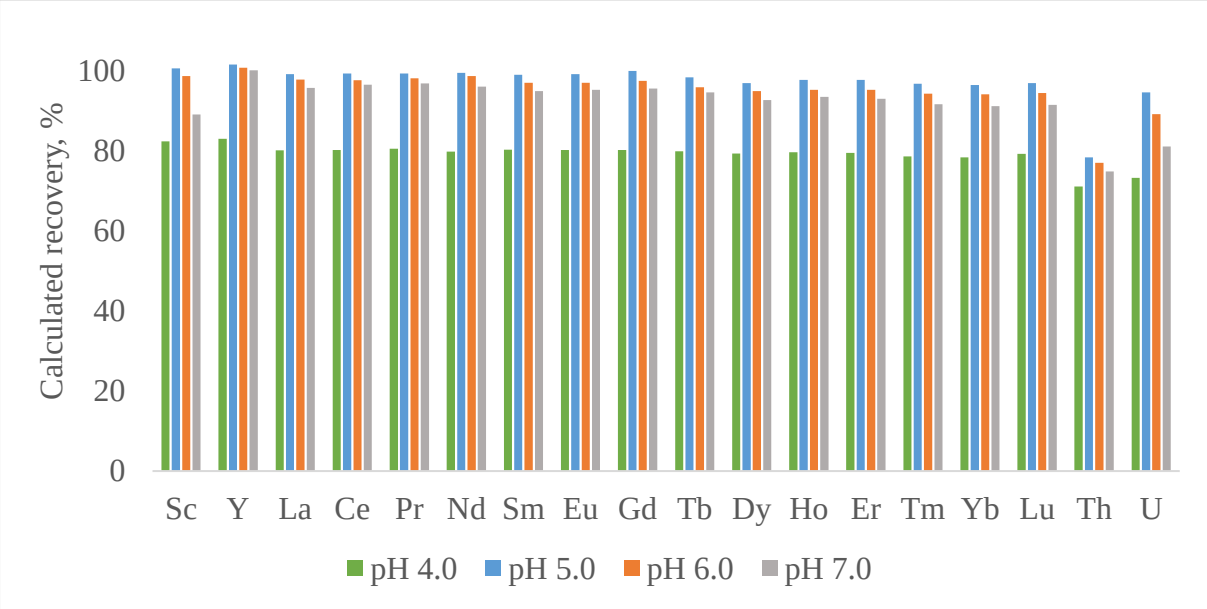

Figure 4.7. The calculated recovery of REEs, Th, and U from the spiked water type 1 (n = 4).

Calculated recovery varied from 74 to 102 %. Since the highest calculated recovery was again obtained for the samples with initial pH 5.0, this pH was chosen for further experiments. Calculated recovery for Th at pH 5.0 was noticeably lower than for the other metals. This means that a larger amount of Th remained uneluted relative to the other metals, given the already demonstrated sub LOD concentrations in preceding SPE steps. For this reason, an elution profile was made to assess if increasing eluent amount would increase amount of eluted Th.

4.12. Elution profiles

Retention strength differs between metals, and elution profiles can provide information on how much eluent is needed for sufficient elution of each metal. To create an elution profile 2 M HNO_3 was applied in increments of 2.00 mL onto the SPE column, until a total volume of 16.00 mL. The elution profiling was started at 2.00 mL to assess if some metals need less than 10 mL to be sufficiently eluted. Spiked water type 1 adjusted to pH 5.0 was used since the highest calculated recovery was exhibited at this pH. The spiking amount of REEs, Th, and U was the same as in the previous experiment, i.e., final concentration of REEs and Th was 594.3 ± 0.2 µg/L each, and concentration of U was 495.2 ± 0.2 µg/L. Figure 4.8 shows the elution profile of REEs, Th, and U. For detailed information on elution data, see Table 6.23 in Appendix.

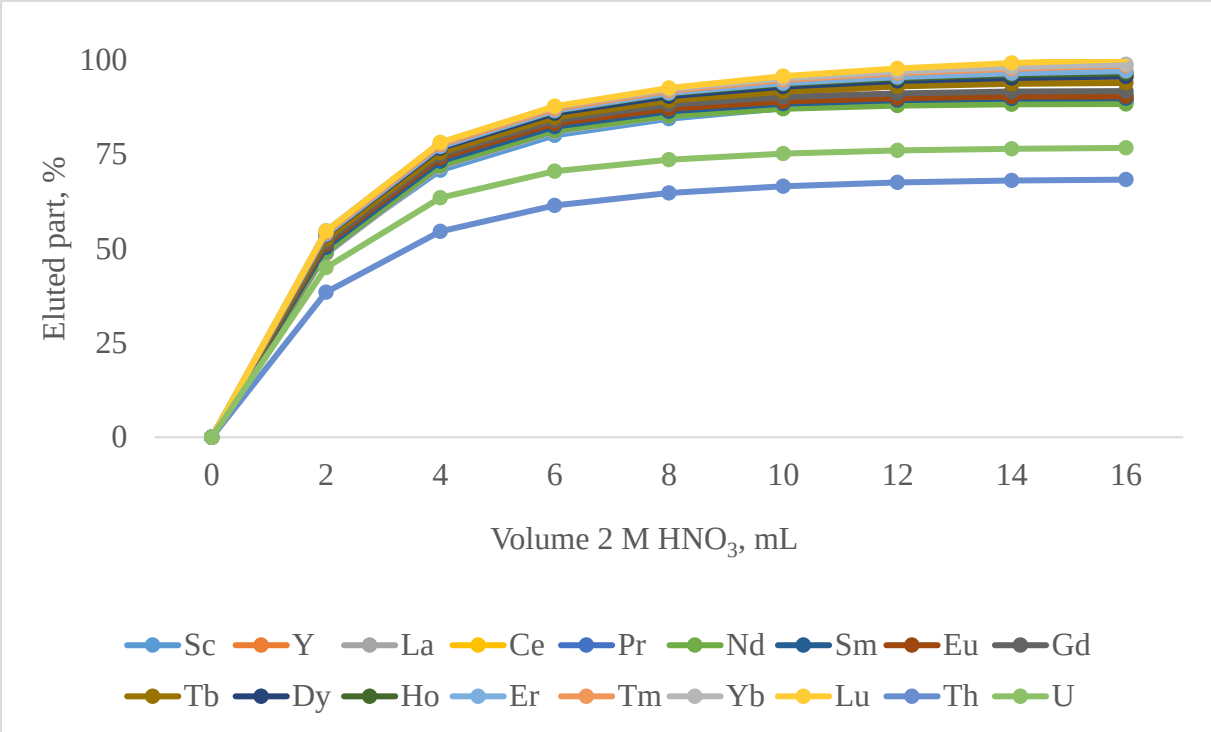

Figure 4.8. Elution profile of REEs, Th, and U by 2 M HNO_3 for sample concentration of REEs and Th of 594.3 ± 0.2 µg/L each, and 495.2 ± 0.2 µg/L of U (n = 4).

The plot above shows that Th and U are the metals with poorest calculated recovery during the SPE procedure. However, for all metals, including Th and U, calculated recovery-changes are miniscule when increasing eluent volume above 10 mL.

To assess if calculated recovery remains the same when concentration of REEs, Th, and U is close to that in actual seawater, samples with the same concentration of 99.6 ± 0.1 ng/L were analysed. Unused SPE columns were utilized to avoid cross contamination, as in this concentration range of analytes, even the slightest contamination would be detrimental. The final eluates were diluted 2 times with water type 1 prior to ICP-MS analysis. Water type 1 was used instead of 0.5 M HNO_3 to reduce acidity of the eluate. Figure 4.9 shows the elution profile of REEs, Th, and U by 2 M HNO_3 for sample concentration of REEs, Th, and U of 99.6 ± 0.1 ng/L each. For detailed information on elution data, see Table 6.24 in Appendix.

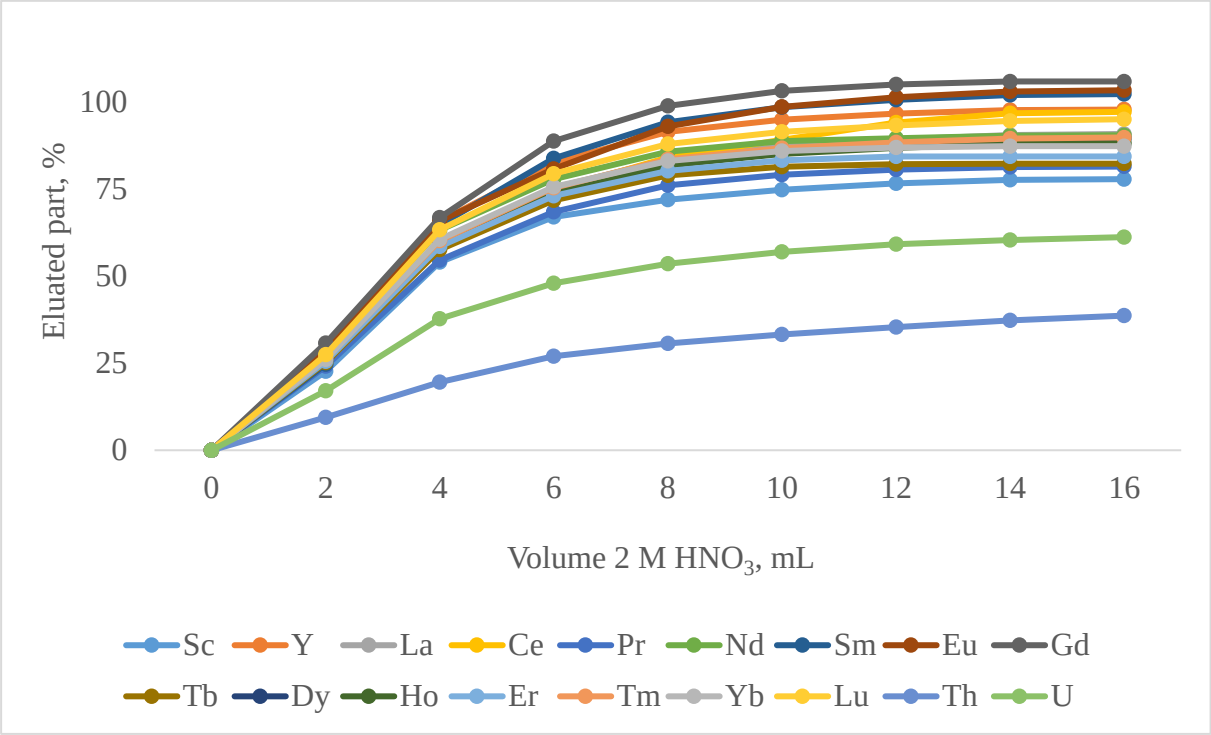

Figure 4.9. Elution profile of REEs, Th, and U by 2 M HNO_3 for sample concentration of REEs, Th, and U of 99.6 ± 0.1 ng/L each (n = 4).

The differences in calculated recovery among REEs are clearly noticeable. Instrument drift and variations in chemical- or physical-chemical properties of REEs will have a larger impact on calculated recovery rates at low- relative to high concentrations of REEs. This could explain the difference in appearance of the two elution profiles.

As these experiments show, Th and U have the poorest calculated recovery regardless of increased eluent volume, and both at high and low sample concentrations. To assess if Th and U could be eluted more efficiently by a more acidic solution, 3 M HNO_3 was used as an eluent. Unused SPE columns were employed, and the final eluates were diluted 2 times with water type 1. The first ICP-MS trial resulted in calculated recovery from 200 to 350 %. The most probable explanation is that the analysed solutions were so acidic that they washed out existing contaminations in the ICP-MS system. Normally, solutions to be analysed by ICP-MS contain 0.5 M HNO_3, while the HNO_3 concentration in these 2 times diluted eluates was approximately 1.5 M. The ICP-MS instrument was rinsed according to the developed procedure described in chapter 3.5, and the measurement of REEs, Th, and U was repeated. The obtained calculated recovery varied from 150 to 250 %. Subsequently, the instrument was rinsed again. Calculated recovery of REEs, Th, and U now varied from 100 to 237 %, (Figure 4.10). For detailed information on elution data, see Table 6.25 in Appendix.

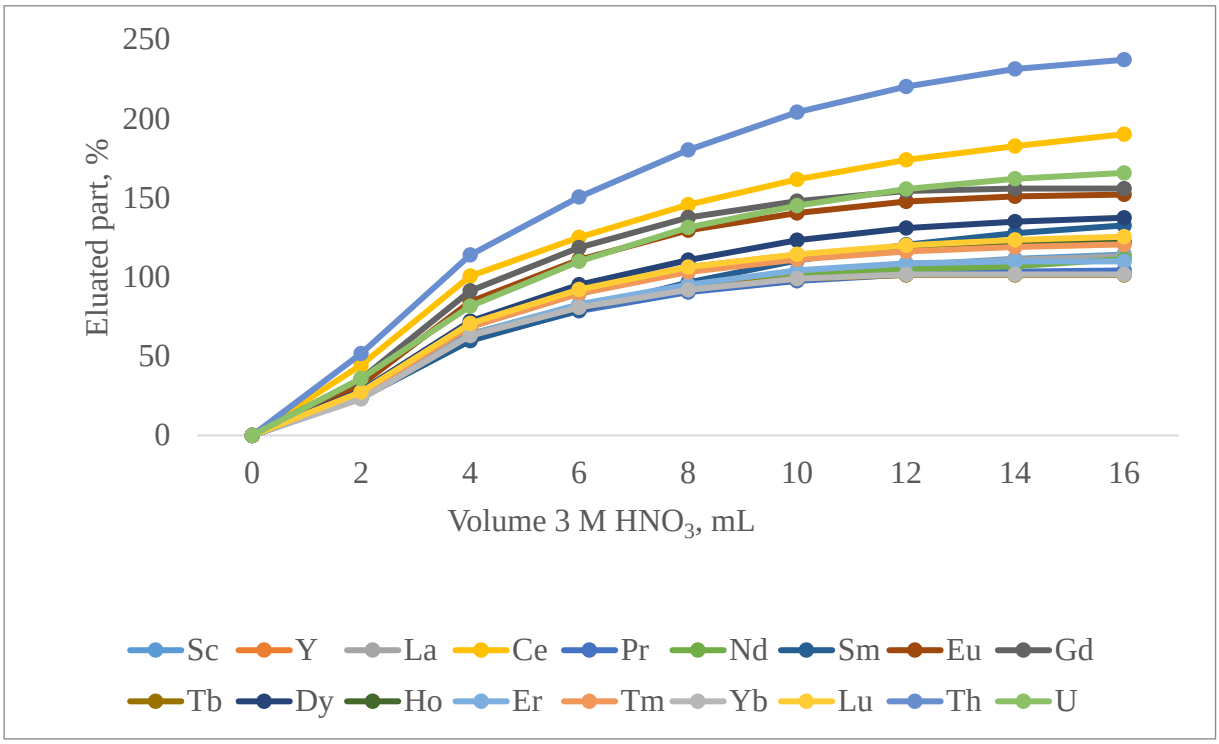

Figure 4.10. Elution profile of REEs, Th, and U by 3 M HNO_3 for sample concentration of REEs, Th, and U of 99.6 ± 0.1 ng/L each (n = 4).

After the first additional rinsing procedure, abnormal calculated recovery improved substantially from the first to the second trial. However, after a second rinsing, calculated recovery was less affected. Since ICP-MS trials are highly resource-intensive, and impact on calculated recovery beyond the first additional rinsing procedure appeared to quickly diminish, further cycles of rinsing and new ICP-MS trials were abandoned. Despite abnormal calculated recovery when using 3 M HNO_3 as an eluent, calculated recovery of Th and U was no longer markedly poorer than that of the other metals. Establishing a procedure using 3 M HNO_3 as an eluent was therefore desirable, but the effect of its high acidity wash-out of ICP-MS system contaminations needed to be eliminated. Obviously, further dilution of the final eluates could resolve this. Hence, the already twice diluted eluates were diluted again 2 times to decrease the acid concentration. However, in most of these solutions, the levels of REEs, Th, and U were under LOD.

Reliable ICP-MS measurements require minimal contamination within the instrument when measuring concentrations in ng/L range. As the previous trials showed, repeated standard rinsing procedures will not always provide sufficiently low levels of contamination. Therefore, thorough cleaning of the inner details of the instrument, i.e., interface cones, by a

specially trained operator is thus needed at regular intervals. Unfortunately, such service is not always available.

The first two elution profiles show that the additional eluted amount of REEs became negligible beyond 10 mL of total eluent. Th and U, though, displayed markedly poorer calculated recovery compared to the other metals. However, Th and U were more effectively eluted when using 3 M HNO_3 as opposed to 2 M HNO_3, but overall calculated recovery profiles became abnormal. Thus, in the next experiment, an eluent of 10.00 mL 2 M HNO_3, which sufficiently elutes REEs, followed by an eluent of 5.00 mL 3 M HNO_3, which increases calculated recovery of Th and U, was used. This was done in an attempt to reduce the impact of highly acidic solutions on ICP-MS: Reduced eluent volume of 3 M HNO_3 and subsequently larger preconcentration effect allows for greater post-SPE dilutions and less acidic final solution for ICP-MS analysis.

4.13. Assessment of matrix cations influence on ICP-MS: Mixing of water type 1 and artificial seawater in different ratios

In the previous experiments, the calculated recovery of metals from the spiked artificial seawater was lower than that from the spiked water type 1. To assess if and in which degree matrix elements influence ICP-MS measurements, analysis of samples with various concentrations of non-analytes should be performed. As extensive dilution of final eluate could render concentrations of analytes below LOQ, four different volume combinations of artificial seawater mixed with water type 1 were prepared. These combinations were: 0 mL seawater and 50.0 mL water type 1 (i.e., only water type 1), 10.0 mL artificial seawater and 40.0 mL water type 1, 25.0 mL artificial seawater and 25.0 mL water type 1, and 50.0 mL artificial seawater and 0 mL water type 1 (i.e., only artificial seawater). All samples were spiked with REEs, Th, and U, so that the final concentration was 1.91 ± 0.01 µg/L of each metal.

The inner details of the ICP-MS, i.e., interface cones, were rinsed by a specially trained person to remove possible cross contaminations in the ICP-MS system.

After SPE, two aliquots were taken from all eluates to prepare solutions diluted 20- and 10 times. To ensure a TDS below ICP-MS tolerance with considerable margin, only the two volume combinations with the least amount of artificial seawater, 0 mL and 10.0 mL, were diluted a mere 5 times.

Since there were two eluents, 10.00 mL 2 M HNO_3 followed by 5.00 mL 3 M HNO_3, the calculated recovery of REEs, Th, and U presents a sum of the recoveries obtained from both eluates.

The ICP-MS results from each sample type were grouped according to dilution degree. This provides an overview of how matrix elements influence the value of measured concentration of REEs, Th, and U. Figures 4.11, 4.12, and 4.13 show the results for 20-, 10- and 5 times diluted aliquots, respectively.

For detailed information on estimated TDS for specific volume combinations and dilutions, see Table 6.26 in Appendix.

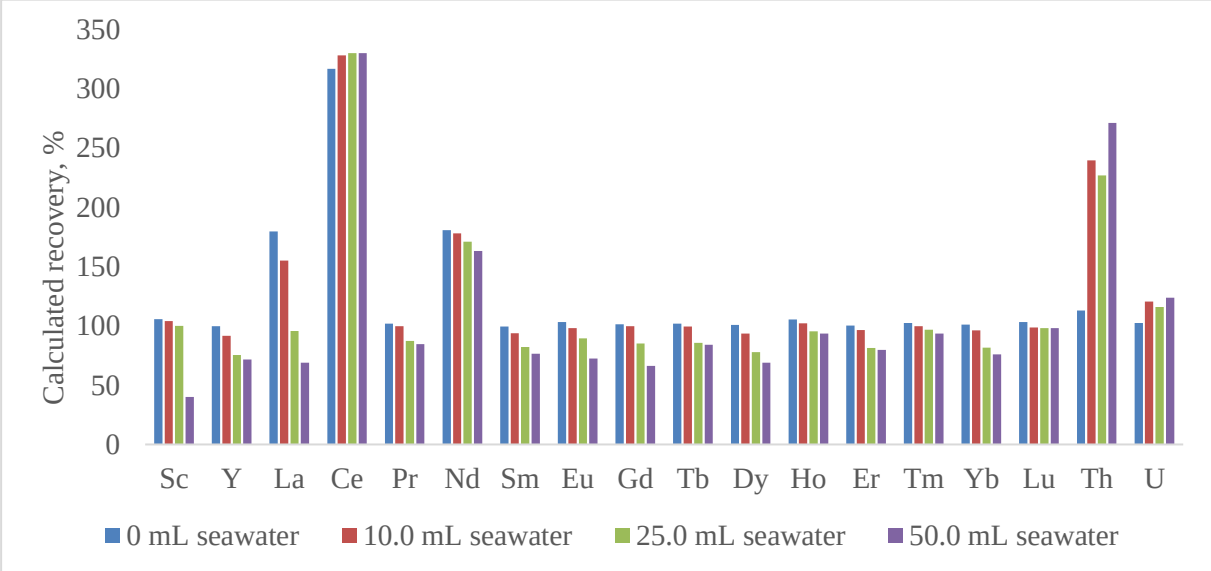

Figure 4.11. Calculated recovery of REEs, Th, and U (%) from 20 times (20x) diluted eluates (n = 4).

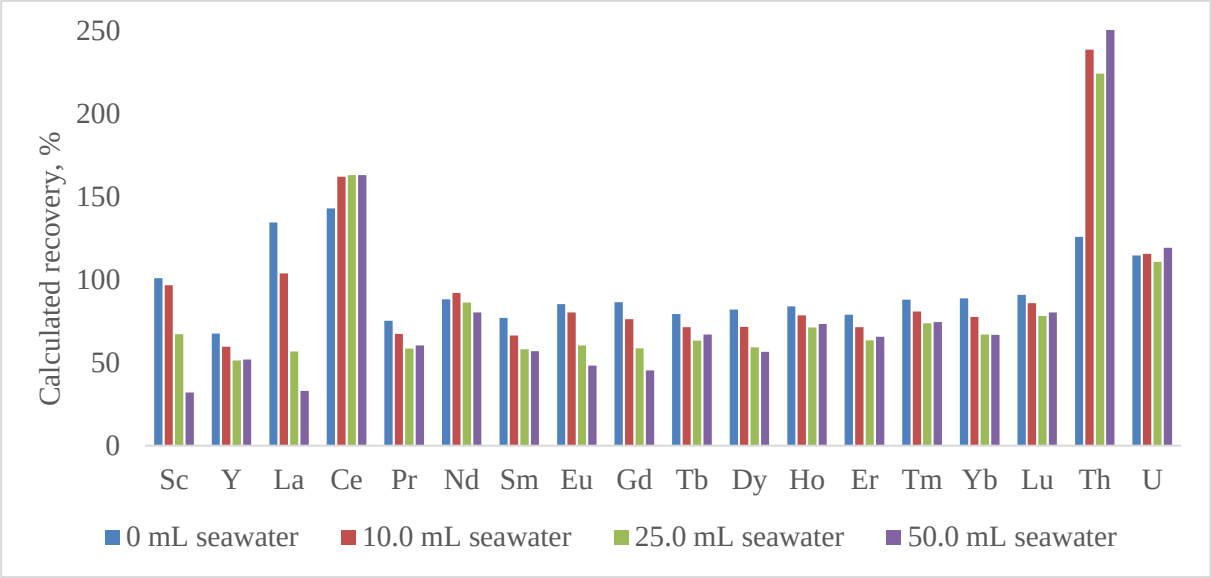

Figure 4.12. Calculated recovery of REEs, Th, and U (%) from 20 times (10x) diluted eluates (n = 4).

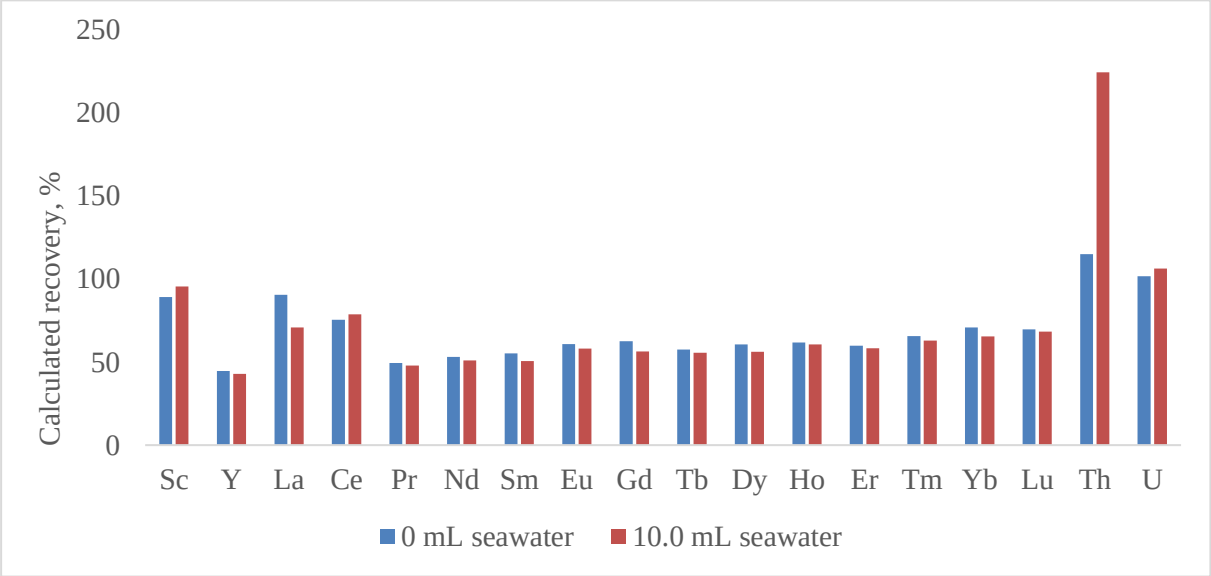

Figure 4.13. Calculated recovery of REEs, Th, and U (%) from 5 times (5x) diluted eluates (n = 4).

For most analytes, calculated recovery decreases with increased concentration of matrix elements in the samples. Even though SPE removes close to 100 % of Na, Mg, Ca, and K from the sample, the absolute amount of these metals in the final eluate is still considerably higher than that of the analytes. This can cause detrimental suppression of the analyte signal in ICP-MS. Therefore, internal standard IS is needed.

Calculated recoveries of above 100 % is due to various sources of contamination, as previously described.

In these experiments, the assumed favourable two-step final elution was performed, using both 2 M and 3 M HNO_3. However, after performing a third SPE procedure with the same column, the resin ceased to completely swell back to its original volume after regeneration. In contrast, when performing final elution with only 2 M HNO_3, resin integrity persisted through at least six SPE procedures. In other words, the lifetime of the columns is much shorter when using 3 M HNO_3 compared to 2 M HNO_3. Because of the resources involved, being able to perform only three SPE procedures with one column is not a viable option. Hence, 3 M HNO_3 was replaced with 2 M HNO_3 when analysing environmental samples.

4.14. Application of the developed method on environmental samples: Results

Seawater samples were collected in Fuengirola, Spain, and Oslo, Norway. By choosing samples from two different water bodies, the Mediterranean Sea and the North Sea, differences in concentrations of REEs, Th, and U were expected. This would provide an interesting basis for analysis. Artificial seawater spiked with REEs, Th, and U (1.91 ± 0.01 µg/L of each metal), and unspiked artificial seawater were also, as controls, analysed in parallel with environmental samples. Two replicates of each environmental sample and two spiked- and two unspiked artificial seawater samples were prepared.

4.14.1. Internal standard application and its influence on the calculated results

The experiment with imitated environmental samples showed that the analyte signal was suppressed by the matrix elements, therefore, IS was used. The element In was chosen as IS, as is common when analysing REEs, Th, and U in seawater [15, 48]. Aliquots of 200 µL were taken from the final eluates to check for possible presence of In prior to addition of IS. Determination of In in all eluates exhibited no detectable traces of it.

Concentrations of REEs, Th, and U in seawater are normally between 0 µg/L and 1 µg/L [6, 14, 17, 23]. IS should preferably be in the same concentration range as the analytes, and its concentration should be high enough to lower the uncertainty of the measurements. Analytes in the 10.00 mL final eluate were preconcentrated 5 times during SPE. Hence, for the 10.00

mL final eluate, spiking amount of In should correspond to an In-concentration of 5.0 µg/L. For simplicity, the same amount of In was used for the 5.00 mL final eluate, thus yielding an In-concentration in the 5.00 mL final eluate of 10.0 µg/L.

Aliquots from each eluate were diluted 20 times prior to ICP-MS measurements. At these dilutions, REEs-, Th-, and U-concentrations were below LOD for replicates of environmental samples. Hence, new aliquots were taken and diluted 10-, 5-, and 2 times. Detected concentrations of all REEs, Th, and U were above LOQ for both replicates of environmental samples only in 2 times diluted aliquots. The net effect of both SPE and eluate dilution prior to ICP-MS was a 2.5-fold preconcentration of analytes.

The calculated recovery of REEs, Th, and U from the spiked artificial seawater, both with and without IS, were compared (Table 4.3).

Table 4.3. Calculated recovery of REEs, Th, and U (%) from the spiked artificial seawater with concentration 1.91 ± 0.01 µg/L of each metal.

Analyte	With IS		Without IS	
	Sample 1	Sample 2	Sample 1	Sample 2
^{45}Sc	94	98	32	16
^{89}Y	88	87	38	20
^{139}La	92	90	58	36
^{140}Ce	91	78	56	22
^{141}Pr	88	82	50	28
^{142}Nd	92	85	52	29
^{152}Sm	111	94	65	37
^{153}Eu	106	98	65	41
^{158}Gd	107	103	61	40
^{159}Tb	97	92	54	35
^{164}Dy	98	99	52	33
^{165}Ho	96	94	51	34
^{166}Er	99	98	49	31
^{169}Tm	99	99	47	30
^{174}Yb	98	97	48	29
^{175}Lu	98	96	51	35
^{232}Th	91	83	43	23
^{238}U	122	131	63	57

The recoveries obtained by using IS are noticeably higher than those without IS. This supports the assumption that matrix elements supress the analyte signal. Furthermore, STD values are substantially higher for the calculated recoveries obtained by analysing the aliquots containing no In. This indicates instrument drift during measurements. These facts support the necessity of IS for seawater analyses, since IS corrects for matrix effects and instrument drift.

The results obtained from the replicates containing In exhibited a recovery of ≥ 82 % for all analytes. U displayed relatively enhanced calculated recovery in all the conducted trials with spiked artificial seawater. However, U does not have any spectral interferences. This means that the enhanced calculated recovery is caused by nonspectral interferences from the matrix.

The results obtained from the analysis of two unspiked artificial seawater samples (using IS) showed presence of Sc, La, Eu, and Gd at concentrations corresponding to 6 and 7 %, 7 and 6 %, 4 and 2 %, and 3 and 3 %, respectively, of the theoretical recovery (100 %) of spiked artificial seawater. Since occurrence of REEs in artificial seawater is unlikely, the detected values were probably caused by contaminations in the ICP-system.

4.14.2. Analyses of environmental samples

In environmental samples, presence of insoluble particles, microorganisms, or organic matter, e.g. algae, can skew analysis. However, it is generally accepted that if no visible differences between natural samples and blanks are apparent, filtration or microwave oven digestion are not necessary. Extra manipulations with a sample can lead to not only loss of analytes, but also introduce contaminations. Figure 4.14 shows seawater samples from Fuengirola, Spain and Oslo, Norway beside the blank consisting of pure 0.5 M HNO_3.

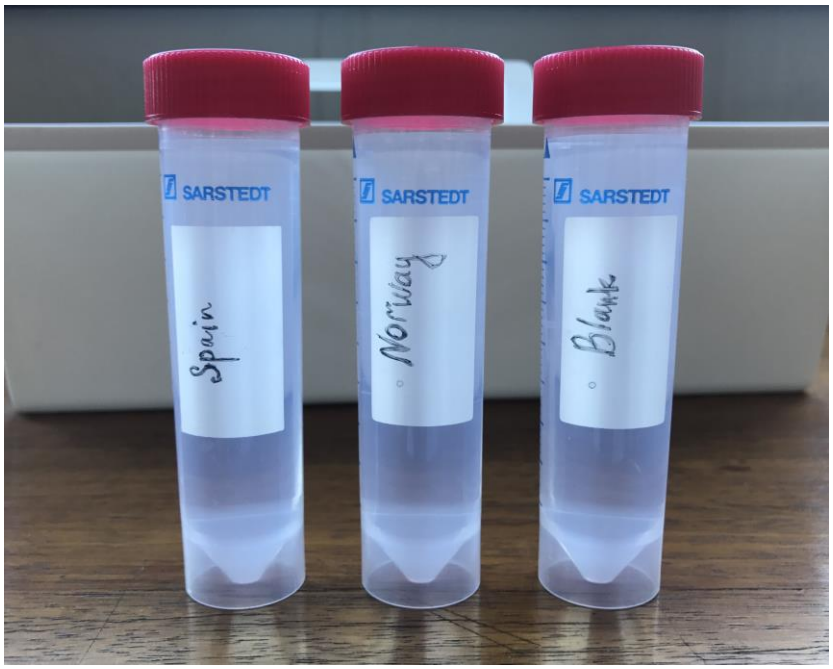

Figure 4.14. Naked eye comparison in day light of the samples from Fuengirola, Spain, and Oslo, Norway with the blank consisting of pure 0.5 M HNO_3.

Since there were no visible differences between the natural samples and the blank, digestion or filtration were not assumed to be necessary. Nevertheless, for seawater from Oslo, Norway, a weak brownish-grey stain was noticed on the outer frit of the SPE column after the second

SPE procedure (Figure 4.15). Figure 4.16 shows the comparison of cross-section views of the outer frits of three SPE setups after the second SPE procedure used for three different samples, i.e., seawater from Fuengirola, Spain, and Oslo, Norway, and unspiked artificial seawater.

Figure 4.15. Cross-section view of the outer frit of the SPE setup after the 2nd SPE procedure of pretreatment of seawater collected in Oslo, Norway.

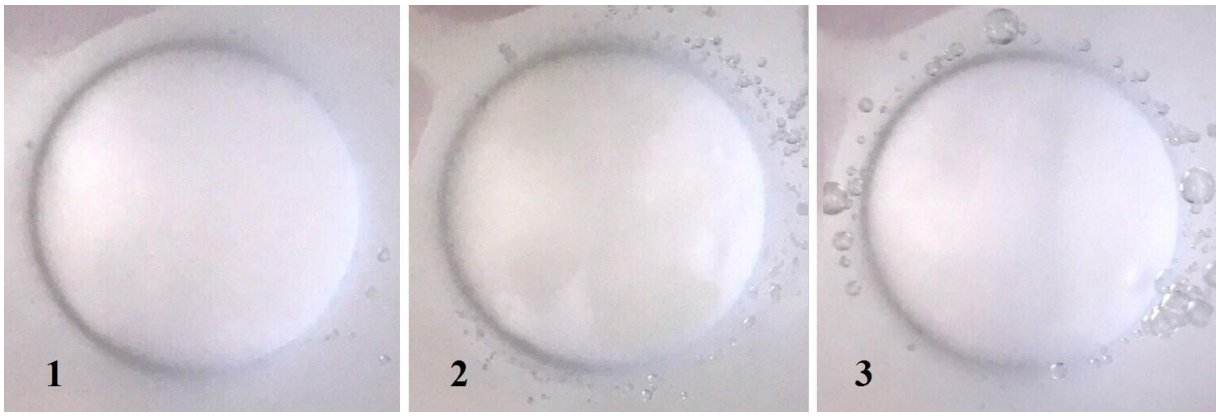

Figure 4.16. Comparison of cross-section views of the outer frits of three SPE setups after the 2nd SPE procedure: 1) Fuengirola, Spain seawater 2) Oslo, Norway seawater 3) Unspiked artificial seawater.

Appearance of the stain on the frit implies presence of algae in the seawater sample from Oslo, Norway. However, if so, the amount of algae was too small to cause clogging. To avoid algae deposition on the frit in future trials, using a filter-paper disk on top of the frit can be a

possible solution of the problem. Because of possible disk impurities, it should be cleansed before loading a sample, i.e., placed on the frit prior to prewashing the SPE column.

Concentration of each analyte was obtained from analysis of the aliquots containing IS. The results are presented in Table 4.4.

Table 4.4. Concentration of REEs, Th, and U (ng/L) in seawater collected in Fuengirola, Spain and Oslo, Norway.

Analyte	Fuengirola, Spain		Oslo, Norway	
	Replicate 1	Replicate 2	Replicate 1	Replicate 2
^{45}Sc	150	142	119	111
^{89}Y	13	10	15.9	19
^{139}La	60	60	86.2	102
^{140}Ce	28	21	27	29
^{141}Pr	3.9	3.0	6.3	6.8
^{142}Nd	11	11	18	21
^{152}Sm	63	50	29	34
^{153}Eu	51	45	45	52
^{158}Gd	49	28	31	35
^{159}Tb	3.5	2.3	3.8	4.1
^{164}Dy	8.8	7.3	9.2	11
^{165}Ho	0.5	0.4	1.1	1.5
^{166}Er	3.1	2.5	4.1	4.1
^{169}Tm	3.3	3.2	4.3	4.6
^{174}Yb	5.8	6.1	7.0	8.3
^{175}Lu	1.2	0.8	1.8	2.2
^{232}Th	4.6	9.3	5.0	7.2
^{238}U	735	910	450	558

U-concentrations in the samples were measured to be between 500 ng/L and 1000 ng/L, whereas a review by Owens from 2011 reports concentrations of U in seawater at around 3000 ng/L [12]. Lowering pH of seawater to 5.0 was expected to transform most of $UO_2(CO_3)_3^{4-}$ to $(UO_2)_2(OH)_2^{2+}$ [30]. However, the discrepancy between this study and Owens' review in terms of measured U-concentrations could suggest that this is not the case.

Conversely, actual differences in U-concentrations between the sampled water bodies could also explain this discrepancy. Future studies should seek to clarify this.

Figure 4.17 presents a comparison of concentrations of REEs and Th in seawater from Fuengirola, Spain, and Oslo, Norway, and concentrations of REEs and Th in seawater from Sanpoku, Japan [17], and Plymouth, UK [21]. Interestingly, even though these water samples are collected from different seawater bodies at widely separated locations, for most of the analytes, the concentrations vary surprisingly little between collection sites, i.e., they are within the 0 – 50 ng/L range. Possible reasons for large variation of concentrations for some analytes are either both naturogenic and anthropogenic causes or differences among applied methods. To find the actual reasons for this, each sample must be analysed using the various methods.

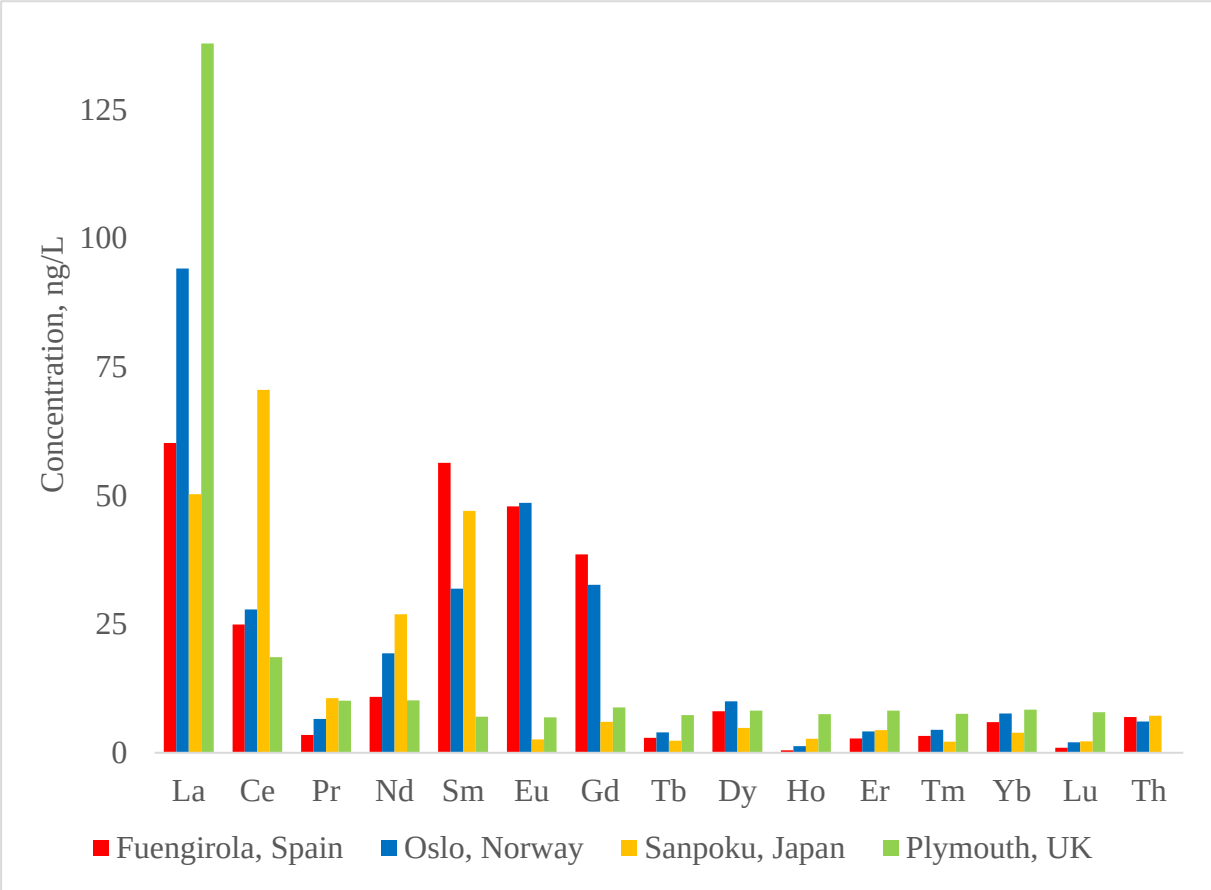

Figure 4.17. Concentrations of REEs and Th in seawater from Fuengirola, Spain, and Oslo, Norway, and concentrations of REEs and Th in seawater from Sanpoku, Japan [17], and Plymouth, UK [21].

5. Conclusion

In this study, a novel off-line SPE method for preconcentration of REEs, Th, and U in seawater, and separation of these metals from main seawater matrix cations, was developed. This novel SPE method successfully reduced TDS to that which was tolerable by ICP-MS, i.e. less than 0.2 %, and from samples of spiked artificial seawater recovery of REEs, Th, and U was equal to or exceeded 82 %. Thus, the newly developed method was applied to determine concentration of REEs, Th, and U in seawater from Fuengirola, Spain, and Oslo, Norway. Comparison between these analyses and measurements performed by other methods showed similar levels of trace elements. This strongly suggests that the method developed in this study is reliable. For acceptable performance of the method, the ICP-MS system must be properly rinsed to avoid cross contaminations from other users. Therefore, a special rinsing procedure was additionally developed in this project. In future work, the novel SPE method can be refined, e.g. by reducing the amount of resin and pumping speed, to decrease cost and labour time. However, the method is already both simple and low-cost compared to existing alternatives. Being mobile, compact, and easy to manage, the SPE method developed in this study therefore holds the potential to become a useful tool for both laboratory and field work.

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Appendix

Table 6.1. Operating conditions for ICP-MS instrument.

Operating parameters	Operating conditions
Plasma conditions	
Incident power (W)	1000
Plasma gas flow rate (L/min)	17.0
Auxiliary gas flow rate (L/min)	1.2
Carrier gas flow rate (L/min)	0.94
Nebulizer	
Sample uptake rate (mL/min)	1.0
Data acquisition	
Measurement mode	Peak hopping
Dwell time (ms/point)	50
Data point (points/peak)	5
Number of scans	15

Table 6.2. Operating conditions for ICP-OES instrument.

Operating parameters	Operating conditions
Plasma conditions	
Incident power (W)	1000
Plasma gas flow rate (L/min)	15.0
Auxiliary gas flow rate (L/min)	1.5
Carrier gas flow rate (L/min)	0.75
Sample introduction	
Sample uptake (s)	30
Rinse Time (s)	10
Pump rate (mL/min)	2.8
Fast pump	On
General settings	
Replicates	3
Replicate time (s)	1.000
Stabilizing time (s)	15

Table 6.3. Measured wavelengths by ICP-OES.

Analyte		Na	Mg	Ca	K
Measured wavelength, nm	I	588.995	285.213		769.897
					766.491
	II		279.800	317.993	
				315.887	

Table 6.4. Preparation of standard solutions, i.e., prepared solutions, for calibration and spiking.

Initial solution	Taken aliquot	Volumetric flask	Prepared solution
Stock solution of REEs and Th (100 µg/mL each)	100 µL	100 mL	100 µg/L
Prepared solution of REEs and Th (100 µg/L)	25.00 mL	50 mL	50 µg/L
Prepared solution of REEs and Th (50 µg/L)	25.00 mL	50 mL	25 µg/L
Stock solution of U (1000 µg/mL)	12.50 mL	50 mL	250 µg/mL
Prepared solution of U (250 µg/mL)	100 µL	250 mL	100 µg/L
Prepared solution of U (100 µg/mL)	25.00 mL	50 mL	50 µg/L
Prepared solution of U (50 µg/L)	25.00 mL	50 mL	25 µg/L
Stock solution In (100 µg/mL)	500 µL	100 mL	500 µg/L
Stock solution of Na and K (10 000 µg/mL each)	12.50 mL	50 mL	2500 µg/mL
Stock solution of Mg and Ca (10 000 µg/mL each)	12.50 mL	50 mL	2500 µg/mL
Stock solution of K (10 000 µg/mL)	12.50 mL	50 mL	2500 µg/mL

Table 6.5. Preparation of calibration solutions for determination of concentration of Na, Mg, Ca, and K.

Metal concentration in prepared calibration solution (200 mL)	Taken aliquot of prepared solution of Na and K (2500 µg/mL each)	Taken aliquot of prepared solution of Mg and Ca (2500 µg/mL each)
12.5 µg/mL	1.00 mL	1.00 mL
25 µg/mL	2.00 mL	2.00 mL
50 µg/mL	4.00 mL	4.00 mL

Table 6.6. Preparation of calibration solutions for determination of concentration of K.

Metal concentration in prepared calibration solution (200 mL)	Taken aliquot of prepared solution of K (2500 µg/mL each)
12.5 µg/mL	1.00 mL
20 µg/mL	2.00 mL
50 µg/mL	4.00 mL

Table 6.7. Preparation of calibration solutions for determination of concentration of REEs, Th, and U in µg/mL range (I).

Metal concentration in prepared calibration solution (100 mL)	Taken aliquot of stock solution of REEs and Th (50 µg/mL each)	Taken aliquot of prepared solution of U (250 µg/mL)
500 µg/L	1.00 mL	200 µL
1000 µg/L	2.00 mL	400 µL
2000 µg/L	4.00 mL	800 µL

Table 6.8. Preparation of calibration solutions for determination of concentration of REEs, Th, and U in µg/mL range (II).

Metal concentration in prepared calibration solution (100 mL)	Taken aliquot of prepared solution of REEs and Th (100 µg/L each)	Taken aliquot of prepared solution of U (100 µg/L)
1.25 µg/L	1.25 mL	1.25 mL
2.50 µg/L	2.50 mL	2.50 mL
5.00 µg/L	5.00 mL	5.00 mL

Table 6.9. Preparation of calibration solutions for determination of concentration of REEs, Th, and U in ng/mL range.

Metal concentration in prepared calibration solution (100 mL)	Taken aliquot of prepared solution of REEs and Th (50 µg/L each)	Taken aliquot of prepared solution of U (50 µg/L)
50 ng/L	100 µL	100 µL
100 ng/L	200 µL	200 µL
200 ng/L	400 µL	400 µL

Table 6.10. Preparation of calibration solutions for determination of concentration of REEs, Th, U, and In in solutions containing IS.

Metal concentration in prepared calibration solution (100 mL)	Taken aliquot of prepared solution of REEs and Th (100 µg/L each)	Taken aliquot of prepared solution of U (100 µg/L)	Taken aliquot of prepared solution of In (500 µg/L)
1.25 µg/L	1.25 mL	1.25 mL	250 µL
2.50 µg/L	2.50 mL	2.50 mL	500 µL
5.00 µg/L	5.00 mL	5.00 mL	1.00 mL

Table 6.11. Preparation of calibration solutions for determination of ICP-MS LOD of REEs, Th, and U.

Metal concentration in prepared calibration solution (100 mL)	Taken aliquot of prepared solution of REEs and Th (25 µg/L each)	Taken aliquot of prepared solution of U (25 µg/L)
25 ng/L	100 µL	100 µL
50 ng/L	200 µL	200 µL
75 ng/L	300 µL	300 µL
100 ng/L	400 µL	400 µL

Preparation of 0.05 M ammonium acetate buffer

To prepare ammonium acetate buffer solutions 0.2 M CH_3COOH and 0.2 M NH_3 solutions were prepared. To prepare 0.2 M CH_3COOH 5.75 mL 100 % (m/v) CH_3COOH was diluted with water type 1 in a 500 mL volumetric flask until the mark. To prepare 0.2 M NH_3 3.99 mL of 28 % (m/v) NH_3 was diluted with water type 1 in a 500 mL volumetric flask until the mark. Table 6.12 shows a preparation scheme of 0.05 M ammonium acetate buffer of pH 5.0 and 6.0.

Table 6.12. Preparation scheme of 0.05 M ammonium acetate buffer of pH 5.0 and 6.0.

pH	0.2 M CH_3COOH	0.2 M NH_3	Diluted with water type 1 to:
5.0	50.0 mL	45.0 mL	200 mL
6.0	50.0 mL	61.2 mL	200 mL

Table 6.13. Analyses of blank (0.5 M HNO_3) for determination of ICP-MS LOD of REEs, Th, and U, 1st approach.

Analyte	Measured concentrations, ng/L									
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
^{45}Sc	21	22	27	28	22	17	16.74	15.06	23.3	17.21
^{89}Y	4.6	4.2	4.2	4.4	4.3	4.2	4.28	4,22	4.5	3.74
^{139}La	4.1	3.9	3.9	4.4	4.1	4.0	4.1	4.0	4.0	4.1
^{140}Ce	2.7	3.0	2.8	2.6	2.9	2.8	2.48	2.8	2.95	2.85
^{141}Pr	1.00	1.14	1.23	1.08	0.99	1.08	1.08	1.22	1.01	1.07
^{142}Nd	0.1	-0.3	-0.1	0.1	0,0	-0.4	0.8	0.3	0.0	0.5
^{152}Sm	-1	1	-1	3	2	0	2	1	4	0
^{153}Eu	-2.3	-1.8	-2.9	-2.6	-1.9	-2.5	-2.3	-2.06	-2.22	-2.5
^{158}Gd	0.7	0.9	0.6	1.2	1.2	0.7	1.28	0.6	0.69	0.62
^{159}Tb	3.420	3.420	3.410	3.400	3.410	3.420	3.410	3.420	3.420	3.420
^{164}Dy	2.4	2.3	1.8	2.3	2.1	2.1	1.7	2.1	2.4	2.2
^{165}Ho	4.43	4.42	4.42	4.43	4.46	4.47	4.45	4.40	4.45	4.41
^{166}Er	2.44	2.42	2.21	2.46	2.29	2.31	2.19	2.46	2.27	2.27
^{169}Tm	-1.38	-1.35	-1.36	-1.33	-1.33	-1.33	-1.39	-1.40	-1.40	-1.33
^{174}Yb	-0.54	-0.26	-0.23	-0.57	-0.47	-0.19	-0.09	-0.36	-0.19	-0.57
^{175}Lu	1.90	1.85	1.81	1.81	1.90	1.83	1.84	1.89	1.85	1.96
^{232}Th	4.9	4.6	5.2	4.3	3.1	3.5	3.3	3.5	3.8	3.5
^{238}U	7.2	7.0	6.7	7.0	6.5	6.6	6.3	6.6	6.5	6.5

Table 6.14. Analyses of blank (0.5 M HNO_3) for determination of ICP-MS LOD of REEs, Th, and U, 2nd approach.

Analyte	Measured concentrations, ng/L			
	1st	2nd	3rd	4th
^{45}Sc	22	18	20	27
^{89}Y	4.4	4.5	4.7	4.7
^{139}La	4.12	3.99	4.10	4.21
^{140}Ce	3.1	2.9	2.9	3.0
^{141}Pr	1.09	1.19	1.04	1.01
^{142}Nd	-0.2	0.5	0.3	-0.1
^{152}Sm	0.7	2.5	0.9	0.7
^{153}Eu	-1.9	-1.4	-2.8	-2.8
^{158}Gd	0.4	1.3	0.6	0.9
^{159}Tb	3.420	3.420	3.420	3.410
^{164}Dy	2.0	2.1	2.0	2.3
^{165}Ho	4.48	4.42	4.47	4.41
^{166}Er	2.3	2.6	2.3	2.3
^{169}Tm	-1.33	-1.36	-1.37	-1.33
^{174}Yb	-0.4	-0.3	-0.3	-0.1
^{175}Lu	1.98	1.89	1.86	1,83
^{232}Th	5	6	6	8
^{238}U	6.8	6.9	7.0	7.4

Table 6.15. Standard deviations for the two approaches of determination of ICP-MS LOD of REEs, Th, and U.

Analyte	STD, ng/L	
	1st Approach	2nd Approach
^{45}Sc	4	3
^{89}Y	0.2	0.1
^{139}La	0.1	0.08
^{140}Ce	0.2	0.1
^{141}Pr	0.08	0.07
^{142}Nd	0.4	0.3
^{152}Sm	2	0.8
^{153}Eu	0.3	0.6
^{158}Gd	0.3	0.3
^{159}Tb	0.007	0.004
^{164}Dy	0.2	0.1
^{165}Ho	0.02	0.03
^{166}Er	0.1	0.1
^{169}Tm	0.03	0.02
^{174}Yb	0.2	0.1
^{175}Lu	0.05	0.06
^{232}Th	0.7	1
^{238}U	0.3	0.3

Table 6.16. Eluted part of Na, Mg, and Ca in the final eluate after SPE using Strata SCX (n = 1).

Samples with different content of HNO_3	Eluted part, %		
	Na	Mg	Ca
Sample 1 (0.25 M)	77	73	55
Sample 2 (0.50 M)	78	75	59
Sample 3 (1.00 M)	78	79	61
Sample 4 (0.50 M)	80	78	64

Table 6.17. Eluted part of Na, Mg, Ca, and K from the loading step at different sample pH values (n = 4). The values are mean ± STD.

Element	Eluted part, %			
	pH 5.0	pH 6.0	pH 7.0	pH 8.0
Na	62.9 ± 0.7	64 ± 1	65 ± 2	63 ± 1
Mg	62.6 ± 0.9	59 ± 2	59 ± 1	61 ± 2
Ca	56.0 ± 0.6	49 ± 1	48 ± 1	52 ± 2
K	58 ± 4	60 ± 1	59.9 ± 0.8	59 ± 1

Table 6.18. Eluted part of Na, Mg, Ca, and K from the buffer-washing step with pH 6.0 buffer at different sample pH values (n = 4). The values are mean ± STD.

Element	Eluted part, %			
	pH 5.0	pH 6.0	pH 7.0	pH 8.0
Na	4.1 ± 0.2	4.5 ± 0.8	4.7 ± 0.8	4.8 ± 0.5
Mg	3.3 ± 0.1	3.6 ± 0.7	3.7 ± 0.8	4.1 ± 0.4
Ca	3.0 ± 0.1	3.1 ± 0.6	3.1 ± 0.7	3.6 ± 0.4
K	3.7 ± 0.1	3.9 ± 0.6	3.9 ± 0.6	4.1 ± 0.4

Table 6.19. Eluted part of Na, Mg, Ca, and K from the final elution step at different sample pH value (n = 4). The values are mean ± STD.

Element	Eluted part, %			
	pH 5.0	pH 6.0	pH 7.0	pH 8.0
Na	0.53 ± 0.02	0.9 ± 0.2	0.9 ± 0.1	0.7 ± 0.2
Mg	3.3 ± 0.1	6 ± 1	7.4 ± 0.7	4.6 ± 0.6
Ca	4.9 ± 0.2	9 ± 2	12 ± 1	7.3 ± 0.9
K	0.45 ± 0.03	0.8 ± 0.2	0.82 ± 0.07	0.7 ± 0.2

Table 6.20. Calculated recovery of REEs, Th, and U, from the final eluate analysed at 10 times dilution (n = 4). The values are mean ± STD.

Analyte	Calculated recovery, %			
	pH 5.0	pH 6.0	pH 7.0	pH 8.0
^{45}Sc	59 ± 3	55 ± 3	54 ± 4	53 ± 1
^{89}Y	18 ± 2	14 ± 2	14 ± 4	12.6 ± 0.7
^{139}La	9 ± 2	2 ± 2	3 ± 4	1.3 ± 0.4
^{140}Ce	9 ± 2	1 ± 2	3 ± 4	0.3 ± 0.4
^{141}Pr	11 ± 2	2 ± 2	4 ± 5	1.1 ± 0.6
^{142}Nd	22 ± 3	7 ± 4	8 ± 7	4.0 ± 0.7
^{152}Sm	27 ± 3	13 ± 4	15 ± 6	13 ± 2
^{153}Eu	19 ± 2	13 ± 4	13 ± 10	12.3 ± 0.6
^{158}Gd	33 ± 3	22 ± 4	25 ± 6	22.1 ± 0.7
^{159}Tb	20 ± 3	13 ± 3	15 ± 5	13.4 ± 0.4
^{164}Dy	42 ± 3	33 ± 4	36 ± 6	32.4 ± 0.6
^{165}Ho	34 ± 3	29 ± 3	3 ± 5	29.9 ± 0.5
^{166}Er	44 ± 3	38 ± 4	40 ± 7	37.4 ± 0.8
^{169}Tm	36 ± 2	33 ± 3	35 ± 5	33.7 ± 0.6
^{174}Yb	46 ± 3	41 ± 4	44 ± 6	40.9 ± 0.6
^{175}Lu	32 ± 2	29 ± 3	31 ± 5	29.3 ± 0.5
^{232}Th	28 ± 2	28 ± 2	28 ± 3	26 ± 2
^{238}U	12 ± 3	2 ± 2	4 ± 5	2 ± 1

Table 6.21. Calculated recovery of REEs, Th, and U, from the final eluate analysed at 20 times dilution (n = 4). The values are mean ± STD.

Analyte	Calculated recovery, %			
	pH 5.0	pH 6.0	pH 7.0	pH 8.0
^{45}Sc	116 ± 10	87 ± 7	101 ± 14	101 ± 10
^{89}Y	72 ± 8	60 ± 10	75 ± 18	77 ± 8
^{139}La	38 ± 8	16 ± 9	32 ± 21	34 ± 8
^{140}Ce	26 ± 9	3 ± 6	18 ± 18	15 ± 8
^{141}Pr	31 ± 9	3 ± 6	19 ± 20	16 ± 9
^{142}Nd	61 ± 9	33 ± 11	49 ± 19	50 ± 9
^{152}Sm	45 ± 8	11 ± 11	30 ± 21	36 ± 11
^{153}Eu	35 ± 8	4 ± 9	22 ± 21	22 ± 9
^{158}Gd	57 ± 7	31 ± 12	50 ± 20	52 ± 8
^{159}Tb	55 ± 8	31 ± 12	50 ± 20	51 ± 8
^{164}Dy	64 ± 8	44 ± 12	62 ± 18	64 ± 7
^{165}Ho	58 ± 9	41 ± 11	61 ± 19	62 ± 9
^{166}Er	70 ± 8	57 ± 11	75 ± 17	76 ± 8
^{169}Tm	81 ± 8	72 ± 11	90 ± 16	92 ± 7
^{174}Yb	103 ± 6	95 ± 12	113 ± 13	114 ± 7
^{175}Lu	106 ± 6	101 ± 12	120 ± 14	121 ± 7
^{232}Th	59 ± 8	68 ± 12	69 ± 7	69 ± 13
^{238}U	26 ± 11	1 ± 2	16 ± 16	8 ± 9

Table 6.22. Calculated recovery of REEs, Th, and U, from the spiked water type 1 (n = 4). The values are mean ± STD.

Analyte	Calculated recovery, %			
	pH 4.0	pH 5.0	pH 6.0	pH 7.0
^{45}Sc	86 ± 6	101 ± 3	99 ± 3	89 ± 3
^{89}Y	86 ± 8	102 ± 3	101 ± 4	100 ± 4
^{139}La	83 ± 8	99 ± 3	98 ± 4	96 ± 4
^{140}Ce	83 ± 9	99 ± 3	98 ± 5	97 ± 5
^{141}Pr	84 ± 9	99 ± 3	98 ± 4	97 ± 4
^{142}Nd	83 ± 8	100 ± 3	99 ± 4	96 ± 4
^{152}Sm	83 ± 8	99 ± 3	97 ± 4	95 ± 4
^{153}Eu	83 ± 8	99 ± 3	97 ± 4	95 ± 4
^{158}Gd	83 ± 9	100 ± 3	98 ± 4	96 ± 4
^{159}Tb	83 ± 8	98 ± 3	96 ± 3	95 ± 4
^{164}Dy	83 ± 8	97 ± 3	95 ± 4	93 ± 4
^{165}Ho	83 ± 8	98 ± 3	95 ± 4	94 ± 4
^{166}Er	83 ± 8	98 ± 3	95 ± 4	93 ± 4
^{169}Tm	82 ± 8	97 ± 3	94 ± 4	92 ± 4
^{174}Yb	82 ± 8	96 ± 3	94 ± 4	91 ± 4
^{175}Lu	82 ± 9	97 ± 3	94 ± 4	92 ± 4
^{232}Th	74 ± 5	78 ± 4	77 ± 2	75 ± 4
^{238}U	76 ± 7	95 ± 4	89 ± 3	81 ± 4

Table 6.23. Elution profile of REEs, Th, and U, eluted by 2 M HNO_3, when initial concentration of each REEs and Th was 594.3 ± 0.2 µg/L, and concentration of U was 495.2 ± 0.2 µg/L in the sample (n = 4). The values are mean ± STD.

Analyte	Increments of 2.00 mL 2 M HNO_3							
	1st (2.00 mL)	2nd (+2.00 mL)	3rd (+2.00 mL)	4th (+2.00 mL)	5th (+2.00 mL)	6th (+2.00 mL)	7th (+2.00 mL)	8th (+2.00 mL)
^{45}Sc	50 ± 5	21 ± 6	9 ± 1	4 ± 1	3 ± 2	2 ± 2	1 ± 1	0.7 ± 0.7
^{89}Y	49 ± 6	24 ± 5	10 ± 1	5 ± 2	3 ± 2	2 ± 2	1 ± 1	1.0 ± 0.5
^{139}La	49 ± 5	23 ± 5	9 ± 1	4 ± 2	2 ± 2	1 ± 2	0.5 ± 0.9	0.1 ± 0.3
^{140}Ce	49 ± 5	23 ± 5	9 ± 1	4 ± 2	2 ± 2	1 ± 2	0.5 ± 0.9	0.2 ± 0.3
^{141}Pr	49 ± 5	23 ± 5	9 ± 1	4 ± 2	2 ± 2	1 ± 2	0.5 ± 0.9	0.1 ± 0.3
^{142}Nd	49 ± 5	23 ± 5	9 ± 1	4 ± 2	2 ± 2	1 ± 2	0.4 ± 0.8	0.04 ± 0.08
^{152}Sm	50 ± 5	23 ± 5	9 ± 1	4 ± 2	2 ± 2	1 ± 2	0.5 ± 0.9	0.1 ± 0.2
^{153}Eu	51 ± 6	23 ± 5	9 ± 1	4 ± 2	2 ± 2	1 ± 2	0.4 ± 0.8	0.1 ± 0.2
^{158}Gd	52 ± 6	23 ± 6	9 ± 1	4 ± 2	2 ± 2	1 ± 2	0.5 ± 0.9	0.1 ± 0.2
^{159}Tb	53 ± 6	23 ± 6	9 ± 1	4 ± 2	2 ± 2	1 ± 2	1 ± 1	0.3 ± 0.5
^{164}Dy	54 ± 6	23 ± 5	9 ± 1	5 ± 2	3 ± 2	2 ± 2	1 ± 1	0.4 ± 0.4
^{165}Ho	54 ± 7	23 ± 6	9 ± 1	5 ± 2	3 ± 2	2 ± 2	1 ± 1	0.4 ± 0.5
^{166}Er	54 ± 7	23 ± 6	10 ± 1	5 ± 2	3 ± 2	2 ± 2	1 ± 1	0.6 ± 0.4
^{169}Tm	54 ± 7	23 ± 6	10 ± 1	5 ± 2	3 ± 2	2 ± 2	1.2 ± 0.9	0.8 ± 0.5
^{174}Yb	55 ± 7	23 ± 6	10 ± 1	5 ± 1	3 ± 2	2 ± 2	1.2 ± 0.9	0.8 ± 0.4
^{175}Lu	55 ± 7	24 ± 6	10 ± 1	5 ± 2	3 ± 2	2 ± 1	1.4 ± 0.9	1.0 ± 0.4
^{232}Th	39 ± 3	16 ± 5	7 ± 1	3.3 ± 0.6	1.8 ± 0.8	1.0 ± 0.8	0.5 ± 0.8	0.3 ± 0.5
^{238}U	45 ± 8	19 ± 8	7.0 ± 0.9	3.1 ± 0.9	2 ± 1	1 ± 1	1 ± 1	0.2 ± 0.5

Table 6.24. Elution profile of REEs, Th, and U, eluted by 2 M HNO_3, when initial concentration of each REEs, Th, and U was 99.6 ± 0.1 ng/L in the sample (n = 4). The values are mean ± STD.

Analyte	Increments of 2.00 mL 2 M HNO_3							
	1st (2.00 mL)	2nd (+2.00 mL)	3rd (+2.00 mL)	4th (+2.00 mL)	5th (+2.00 mL)	6th (+2.00 mL)	7th (+2.00 mL)	8th (+2.00 mL)
^{45}Sc	22.6 ± 0.5	31 ± 2	13.0 ± 0.5	4.9 ± 0.7	2.9 ± 0.9	1.8 ± 0.7	1.0 ± 0.5	0.22 ± 0.09
^{89}Y	27 ± 3	38 ± 7	17 ± 4	9 ± 2	4 ± 1	1.7 ± 0.6	1.0 ± 0.3	0.17 ± 0.06
^{139}La	26 ± 4	34 ± 5	16 ± 3	9 ± 2	4 ± 1	1.9 ± 0.6	1.3 ± 0.3	0.3 ± 0.1
^{140}Ce	25 ± 4	33 ± 5	16 ± 3	10 ± 2	5 ± 1	4.9 ± 0.6	2.7 ± 0.4	0.4 ± 0.1
^{141}Pr	24 ± 4	30 ± 5	14 ± 3	8 ± 2	3 ± 1	1.5 ± 0.5	0.8 ± 0.3	0.10 ± 0.04
^{142}Nd	27 ± 4	36 ± 5	15 ± 3	8 ± 2	3 ± 1	0.8 ± 0.5	0.8 ± 0.8	0.08 ± 0.08
^{152}Sm	25 ± 5	40 ± 6	14 ± 4	10 ± 2	4 ± 1	2.1 ± 0.7	1.4 ± 0.4	0.2 ± 0.1
^{153}Eu	29 ± 8	37 ± 8	15 ± 5	13 ± 3	6 ± 2	2.8 ± 0.9	1.6 ± 0.6	0.4 ± 0.1
^{158}Gd	31 ± 6	36 ± 7	21 ± 4	11 ± 2	4 ± 1	1.8 ± 0.7	0.9 ± 0.4	not detected
^{159}Tb	25 ± 5	32 ± 5	14 ± 3	7 ± 2	3 ± 1	0.8 ± 0.5	0.2 ± 0.1	not detected
^{164}Dy	26 ± 5	33 ± 5	15 ± 3	8 ± 2	4 ± 1	1.8 ± 0.5	1.2 ± 0.3	0.18 ± 0.09
^{165}Ho	26 ± 3	33 ± 5	15 ± 2	8 ± 1	3.3 ± 0.6	1.7 ± 0.3	1.1 ± 0.2	0.16 ± 0.07
^{166}Er	25 ± 5	33 ± 5	15 ± 3	7 ± 2	3 ± 1	1.1 ± 0.5	0.1 ± 0.3	not detected
^{169}Tm	26 ± 4	34 ± 5	15 ± 3	8 ± 2	3 ± 1	1.7 ± 0.5	1.1 ± 0.3	0.3 ± 0.1
^{174}Yb	26 ± 4	34 ± 5	15 ± 3	7 ± 2	3 ± 1	1.0 ± 0.5	0.4 ± 0.3	not detected
^{175}Lu	27 ± 5	36 ± 5	16 ± 3	9 ± 2	4 ± 1	1.8 ± 0.5	1.1 ± 0.3	0.5 ± 0.1
^{232}Th	9 ± 1	10 ± 1	7.4 ± 0.9	3.6 ± 0.9	2.6 ± 0.6	2.1 ± 0.2	1.9 ± 0.4	1.4 ± 0.1
^{238}U	17 ± 2	21 ± 2	10.2 ± 0.7	5.6 ± 0.7	3.4 ± 0.9	2.2 ± 0.5	1.2 ± 0.4	0.8 ± 0.1

Tabell 6.25. Elution profile of REEs, Th, and U, eluted by 3 M HNO_3, when initial concentration of each REEs, Th, and U was 99.6 ± 0.1 ng/L in the sample (n = 4). The values are mean ± STD.

Analyte	Increments of 2.00 mL 3 M HNO_3							
	1st (2.00 mL)	2nd (+2.00 mL)	3rd (+2.00 mL)	4th (+2.00 mL)	5th (+2.00 mL)	6th (+2.00 mL)	7th (+2.00 mL)	8th (+2.00 mL)
^{45}Sc	24 ± 3	38 ± 1	17 ± 1	13 ± 4	8.5 ± 0.2	6.6 ± 0.9	4 ± 2	3 ± 2
^{89}Y	26 ± 3	45 ± 4	21 ± 2	14.3 ± 0.9	8 ± 2	5 ± 1	2 ± 1	1 ± 1
^{139}La	24 ± 2	37 ± 4	19 ± 1	13.5 ± 0.9	8 ± 2	6 ± 1	3.4 ± 0.9	2 ± 1
^{140}Ce	45 ± 11	56 ± 5	25 ± 1	21 ± 4	16 ± 1	12.3 ± 0.8	9 ± 1	8 ± 1
^{141}Pr	24 ± 2	37 ± 4	18 ± 2	11.0 ± 0.6	7 ± 2	4 ± 1	2 ± 1	1 ± 1
^{142}Nd	24 ± 3	37 ± 6	19 ± 2	12.2 ± 0.3	8 ± 3	5 ± 2	2 ± 2	4.6 ± 0.6
^{152}Sm	24 ± 9	36 ± 4	19 ± 5	17 ± 5	14 ± 7	10 ± 3	7 ± 2	5 ± 1
^{153}Eu	32 ± 2	52 ± 4	27 ± 1	19 ± 2	11 ± 2	7 ± 2	3 ± 1	1 ± 1
^{158}Gd	36 ± 1	56 ± 4	27 ± 2	18.9 ± 0.7	10 ± 4	6 ± 3	2 ± 2	not detected
^{159}Tb	24 ± 3	40 ± 5	18 ± 3	10.9 ± 0.8	6 ± 3	2 ± 2	3 ± 2	not detected
^{164}Dy	28 ± 1	44 ± 4	23.0 ± 0.1	16 ± 2	12 ± 2	7.6 ± 0.7	4.1 ± 0.9	2.5 ± 0.5
^{165}Ho	27 ± 1	42 ± 3	21 ± 1	14 ± 2	8 ± 1	5.4 ± 0.7	3.1 ± 0.3	1.7 ± 0.4
^{166}Er	25 ± 2	39 ± 5	19 ± 2	12.1 ± 0.1	9.2 ± 0.2	4 ± 2	1 ± 2	not detected
^{169}Tm	27 ± 1	42 ± 3	21 ± 1	14 ± 2	7.8 ± 0.7	5.2 ± 0.5	2.9 ± 0.2	1.5 ± 0.3
^{174}Yb	23 ± 4	40 ± 5	18 ± 3	11.0 ± 0.4	7 ± 1	3 ± 3	3 ± 2	not detected
^{175}Lu	27 ± 1	43 ± 2	21.4 ± 0.2	14 ± 2	8.1 ± 0.4	5.71 ± 0.03	3.3 ± 0.1	2.1 ± 0.1
^{232}Th	52 ± 2	62 ± 9	37 ± 2	30 ± 4	24 ± 2	16 ± 1	11.1 ± 0.7	5.8 ± 0.2
^{238}U	36 ± 1	46 ± 2	28 ± 1	21 ± 2	14 ± 2	11 ± 1	6.5 ± 0.8	4 ± 1

Table 6.26. Estimated levels of TDS (%) in the final eluates of the samples with different volume combinations of water type 1 and artificial seawater based on the calculated TDS of artificial seawater described in chapter 4.10.1.

Volume of artificial seawater in the initial sample	Dilution		
	20x	10x	5x
10.0 mL	1.5×10^{-3}	3.0×10^{-3}	6.0×10^{-3}
25.0 mL	3.8×10^{-3}	7.5×10^{-3}	
50.0 mL	7.5×10^{-3}	1.5×10^{-2}	

Table 6.27. Calculated recovery of REEs, Th, and U (%), from 20 times (20x) diluted eluates (n = 4). The values are mean ± STD.

Analyte	20x dilution			
	0 mL seawater	10.0 mL seawater	25.0 mL seawater	50.0 mL seawater
^{45}Sc	106 ± 5	103 ± 8	100 ± 6	40 ± 2
^{89}Y	100 ± 4	92 ± 1	76 ± 1	72 ± 16
^{139}La	180 ± 6	155 ± 4	96 ± 19	69 ± 18
^{140}Ce	317 ± 15	328 ± 27	330 ± 21	330 ± 21
^{141}Pr	102 ± 3	100 ± 3	87 ± 1	85 ± 14
^{142}Nd	181 ± 2	178 ± 4	171 ± 1	163 ± 9
^{152}Sm	99 ± 2	94 ± 2	82 ± 2	77 ± 7
^{153}Eu	103 ± 5	98 ± 1	90 ± 7	73 ± 7
^{158}Gd	101 ± 3	100 ± 1	85 ± 7	66 ± 1
^{159}Tb	102 ± 3	100 ± 2	86 ± 1	84 ± 7
^{164}Dy	101 ± 1	94 ± 1	78 ± 4	69 ± 7
^{165}Ho	105 ± 4	102 ± 4	95 ± 4	94 ± 4
^{166}Er	100 ± 1	96 ± 1	81 ± 1	80 ± 5
^{169}Tm	102 ± 2	100 ± 4	97 ± 4	94 ± 3
^{174}Yb	101 ± 3	96 ± 1	82 ± 3	76 ± 3
^{175}Lu	103 ± 2	99 ± 4	98 ± 4	98 ± 4
^{232}Th	113 ± 2	239 ± 1	227 ± 13	271 ± 16
^{238}U	102 ± 3	121 ± 6	116 ± 2	124 ± 4

Table 6.28. Calculated recovery of REEs, Th, and U (%), from 10 times (10x) diluted eluates (n = 4). The values are mean ± STD.

Analyte	10x dilution			
	0 mL seawater	10.0 mL seawater	25.0 mL seawater	50.0 mL seawater
^{45}Sc	101 ± 4	97 ± 10	67 ± 39	32.1 ± 28
^{89}Y	68 ± 12	60 ± 1	52 ± 1	52 ± 53
^{139}La	134 ± 5	103 ± 5	57 ± 20	33 ± 67
^{140}Ce	143 ± 8	162 ± 30	163 ± 40	163 ± 8
^{141}Pr	75 ± 10	67 ± 2	58 ± 2	60 ± 49
^{142}Nd	88 ± 4	92 ± 1	86 ± 2	80 ± 3
^{152}Sm	77 ± 5	66 ± 1	58 ± 1	57 ± 8
^{153}Eu	85 ± 1	80 ± 1	60 ± 8	48 ± 34
^{158}Gd	86 ± 9	76 ± 1	59 ± 8	45 ± 41
^{159}Tb	79 ± 7	71 ± 2	63 ± 2	67 ± 46
^{164}Dy	82 ± 4	72 ± 1	59 ± 3	57 ± 38
^{165}Ho	84 ± 9	79 ± 3	71 ± 3	73 ± 43
^{166}Er	79 ± 5	71 ± 1	63 ± 1	66 ± 20
^{169}Tm	88 ± 6	81 ± 3	74 ± 3	75 ± 40
^{174}Yb	89 ± 3	78 ± 1	67 ± 2	67 ± 34
^{175}Lu	91 ± 4	86 ± 3	78 ± 3	80 ± 37
^{232}Th	126 ± 9	238 ± 19	223 ± 13	267 ± 25
^{238}U	114 ± 4	116 ± 5	111 ± 2	119 ± 3

Table 6.29. Calculated recovery of REEs, Th, and U (%), from 5 times (5x) diluted eluates (n = 4). The values are mean ± STD.

Analyte	5x dilution	
	0 mL seawater	10.0 mL seawater
^{45}Sc	89 ± 18	95 ± 11
^{89}Y	45 ± 13	43 ± 1
^{139}La	91 ± 10	71 ± 6
^{140}Ce	75 ± 24	79 ± 20
^{141}Pr	50 ± 20	48 ± 2
^{142}Nd	53 ± 9	51 ± 1
^{152}Sm	55 ± 18	51 ± 1
^{153}Eu	61 ± 10	58 ± 2
^{158}Gd	63 ± 19	56 ± 2
^{159}Tb	58 ± 8	56 ± 2
^{164}Dy	61 ± 1	56 ± 1
^{165}Ho	62 ± 11	61 ± 3
^{166}Er	60 ± 7	58 ± 2
^{169}Tm	66 ± 12	63 ± 2
^{174}Yb	71 ± 13	65 ± 1
^{175}Lu	70 ± 14	68 ± 3
^{232}Th	115 ± 3	225 ± 18
^{238}U	102 ± 9	106 ± 5