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Rikhotso, Xikhongelo Valentia. (2023). Determination of U and Th Radioisotopes in environmental samples by ICP-QMS. [Master's dissertation, University of the Witwatersrand, Johannesburg]. https://hdl.handle.net/10539/41689

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DETERMINATION OF U AND Th RADIOISOTOPES IN ENVIRONMENTAL SAMPLES BY ICP-QMS

by

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(1176956)

A Master's dissertation submitted to the Faculty of Science, University of the Witwatersrand in fulfilment of the requirements of the degree of Master of Science.

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Co-Supervisor: Dr. James Sehata

JULY 2023

CANDIDATE'S DECLARATION (SIGNED)

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.



_____

(Signature of candidate)

24th day of JULY 2023 at Randburg

DEDICATION

This dissertation is dedicated to my parents. For their unending love, encouragement, and support.

AKNOWLEDGEMENTS

- I would like to thank all the people who contributed into making this Postgraduate Journey a success.
- I would like to thank my supervisors Prof. Luke Chimuka and Dr James Sehata for allowing me to be under their supervision, for the guidance, encouragements, and support during my postgraduate studies and for helping me make this a successful journey.
- To my manager Dr James Tshilongo for encouraging me to pursue this postgraduate studies. To my colleagues, Miss Mpho Ramabulana and Mrs Happy Mabowa for assisting with the columns. To miss Hlengiwe Mnculwane and Mrs Lebohang Hlatshwayo who assisted with the project ideas. To Mr Napo Ntsasa who assisted in obtaining the certified reference materials.
- To the Hydrometallurgy discipline for assisting with the processing of the mine tailing samples. To the ACD team and the fellow MSC students for their endless support and motivations.
- To my family who provided endless support and encouragement throughout the studies.
- I would also like to acknowledge the financial support from Mintek and National Research Foundation (NRF).
- I would like to thank God for the gift of life and for allowing me to walk this journey.

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ABBREVIATIONS

Ac	: Actinium
AMS	: Accelerator mass spectrometry
BEC	: Background Equivalent Concentration
Bi	: Bismuth
Bq	: Becquerel
BV	: Bed volume
CRMs	: Certified Reference Materials
d	: Days
GDMS	: Glow discharge mass spectrometry
h	: Hours
ICP-MS	: Inductively coupled plasma mass spectrometry.
ICP-QMS	: Quadrupole inductively coupled plasma mass spectrometry.
ICP-SF-MS	: Inductively coupled plasma mass spectrometry sector field focusing.
JRC	: Joint research centre
KED	: Kinetic energy discrimination
LA-ICP-MS	: Laser ablation inductively coupled plasma mass spectroscopy.
LoD	: Limit of detection

LGC : Laboratory of the Government Chemist

LSC : Liquid scintillation counting

m : Minutes

mBq : Megabecquerel

mg : Milligram

mL : Millilitre

MΩ : Million Ohms

NAA : Neutron activation analysis

nBq : Nano Becquerel

Nist : National Institute of Standards and Technology

Pa : Protactinium

Pb : Lead

Po : Polonium

PTFE : Polytetrafluoroethylene

Ra : Radium

RIMS : Resonance ionization mass spectrometry

Rn : Radon

s : Seconds

SIMS : Secondary ion mass spectrometry

Th	: Thorium
Tl	: Thallium
TIMS	: Thermal ionization mass spectrometry
U	: Uranium
y	: Years
µBq	: Micro Becquerel
µS	: Microseconds

CHAPTER 1: INTRODUCTION

1.1 Background

Radioactive isotopes of uranium (U) and thorium (Th) decays by alpha, beta, or gamma particles to form stable nuclei. In the process of the decay series, daughter isotopes are formed which contribute to the sources of radioisotopes in the environment. There are several sources of radioactive isotopes. Some radioactive isotopes are present as cosmic radiation, terrestrial radiation such as thorium and uranium which are naturally occurring alpha-emitting elements found naturally in rocks, sediments and soil whose decay led to the formation of radioisotopes and a toxic heavy metal lead (Pb). Uranium and thorium also occur in trace amounts in the environment (Valkovic, 2000; Harb, 2004). Others are generated by decaying radioactive nuclides dissolved in solutions from the ^{238}U and ^{232}Th decay chains (Kónya and Nagy, 2012). Some radioisotopes are introduced into the environment by human activities including processes of nuclear fuel cycle, waste storage, mining, medical applications, and a variety of other systems. Many of these radioisotopes can be anthropogenically generated and accidentally released in the environment leading to radioactive contamination and associated health risks (Betti, 2000; Aydin *et al*., 2020).

Radioisotopes are also a source of contamination for the environment as they are brought to the surface as waste disposal from mining and industrial activities. These radioisotopes are also formed by the decay of actinides such as ^{238}U which has a decay series leading to other radioisotopes formation (Whicker and Schultz, 1982). These radioisotopes become exposed to weathering and leaching with water. This enhances the natural radiation which may lead to elevated radiation exposure for people living near contaminated environments (Darda *et al*., 2021). Radioisotopes are chemically hazardous and accumulate mostly in the bones, liver, kidneys, and other human organs, causing haematological, neurological, and immunological system illnesses, as well as leukaemia and other health problems. Thus, radioisotope analysis is necessary for industries that deal with environmental monitoring, decontamination, and the remediation of environmental contamination (Zoriy, 2005).

1.2 Types of radiation

There are three most common types of radioactive decay an unstable nucleus can undergo: alpha (α) decay, beta (β) decay, and gamma (γ) decay. Other decay modes may include positron emission and electron capture (Podgorsak and Podgoršak, 2014). However, these will not be discussed any further in this thesis as the focus will be on the alpha radiation. Even though thorium has radioisotopes that are beta emitters, the aim of the study is to determine the Th and U radioisotopes that are producing alpha particles.

Alpha radiation is a decay mode for heavy radioisotopes such as ^{238}U and ^{232}Th. The heavy radioisotopes have excess energy which is removed during alpha radiation by emitting a helium nucleus called alpha (α) particle. Alpha radiation pose little danger to humans due to its low penetrating power to the skin (Lehto and Hou, 2011). However, it can have harmful effects when ingested.

1.3 Problem Statement

The decay of uranium and thorium leads to the formation of many radioisotopes which leads to enhanced radioisotopes concentrations in the environment. These radioisotopes are present in trace amounts in the environment and can be anthropogenic generated and accidentally released into the environment. Some radioisotopes are introduced into the environment by human activities including processes of nuclear fuel cycle, waste storage, mining, medical applications, and other variety of systems. Furthermore, the radioisotopes of U (^{234}U, ^{235}U, ^{238}U) and Th, (^{232}Th, ^{234}Th and ^{228}Th) may cause contamination to the environment hence there is a need for their monitoring. In a South African perspective, there are limited analytical methods that can extract these radioisotopes and separate them. Most of these analytical methods are from the developed countries. The Quadrupole inductively coupled mass spectrometry (ICP-QMS) has the capabilities of quantifying these radioisotopes of U and Th at a shorter period of time and at lower costs compared to other techniques.

2.1 Radioisotopes of Uranium and Thorium

2.1.1 Uranium background

Uranium is a naturally occurring heavy metal that can be found in trace amounts in rocks, soils, and water. Uranium is dispersed in the environment by geological processes, such as wind, and rain. Mining and refining procedures, which produce wastes such as mill tailings, can also be used to remove, and concentrate uranium. Uranium consists of three alpha radioactive isotopes with abundances of ^{238}U (99.27%), ^{235}U (0.72%) and ^{234}U (0.01%). In addition, uranium also has three artificial isotopes that are long-lived, ^{232}U ($t_{1/2}$: 69 years), ^{233}U ($t_{1/2}$: 160000 years) and ^{236}U ($t_{1/2}$: 23.420 million years) (Popov, 2016).

The decay of ^{238}U (Figure 1) and human activities from modern industry such as chemical waste disposals are among the sources of human exposure to radiation and need to be monitored to assess possible health risks. These human activities enhance the uranium concentration in the natural environment which increases exposure for people living in such an environment (Boryło, 2013; Popov, 2016). Furthermore, high exposure or intake of uranium can cause damage to the kidney and other harmful effects on the lungs and bone marrow (Boryło, 2013; Popov, 2016).

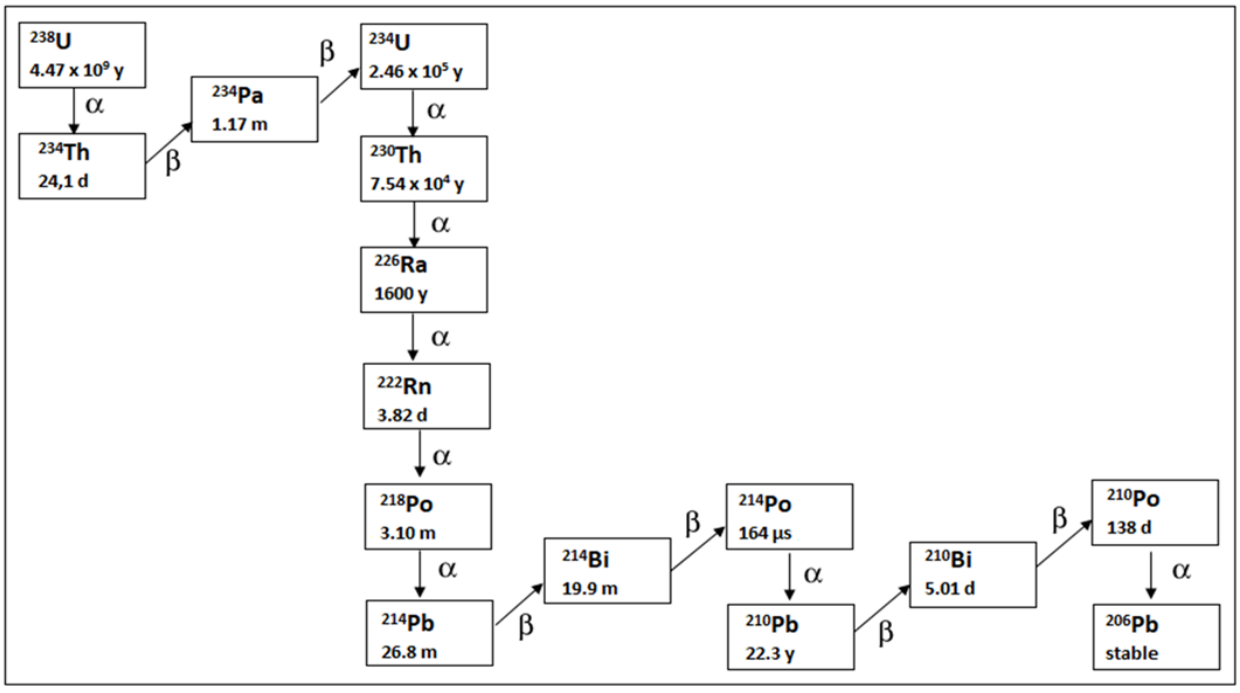


Figure 1: Decay chain of ^{238}U (Costa *et al*., 2015)

2.1.2 Thorium background

The naturally occurring, slightly radioactive metal thorium exist mostly with uranium, due to the decay of uranium. Thorium has many isotopes, with ^{232}Th being the natural isotope and most abundant. Thorium isotopes are available in the thorium, uranium, and actinium series. In the uranium series thorium has two isotopes, ^{230}Th ($t_{1/2}$: 7.54104 years) which is α-emitting and ^{234}Th ($t_{1/2}$: 24.10 days) which is β-emitting. In the thorium series there's ^{232}Th ($t_{1/2}$: 1.411010 year) and ^{228}Th ($t_{1/2}$: 1.913 years) which are both α-emitting and there are β-emitting ^{231}Th ($t_{1/2}$: 25.52 hours) and α-emitting ^{227}Th ($t_{1/2}$: 18.7 days) in the actinium series (Bhatti *et al*., 2012; Costa *et al*., 2015). Due to their relatively long half-lives, high natural abundance, activity concentration and α-particle radiation, the isotopes ^{232}Th, ^{230}Th, and ^{228}Th are particularly important among these isotopes. Thorium is considered toxic due to its decay chain (Figure 2) which produces radioactive isotopes such as ^{228}Ra and ^{208}Pb (Jia *et al*., 2008; Mas *et al*., 2020). As a result, sensitive and reliable thorium determination methods in environmental samples are required to assess the health impacts of thorium exposure.

Most analytical techniques, such as fluorimetry, spectrophotometry, α-spectrometry, β-spectrometry, inductively coupled plasma-mass spectrometry (ICP-MS), neutron activation analysis (NAA), etc., can be used to determine thorium in gram-size soil samples. The concentrations of thorium (^{232}Th) in soil were high (30.2 to 48.6 Bq kg^{-1}) due to the extreme fractionation of thorium between soil (sediment) and water. However, the concentrations of thorium in water, on the other hand, are so low that most of the techniques discussed in Section 2.2 have a hard time determining them. As a result, less data on the concentration of thorium in natural water has been quantified (Jia *et al*., 2008).

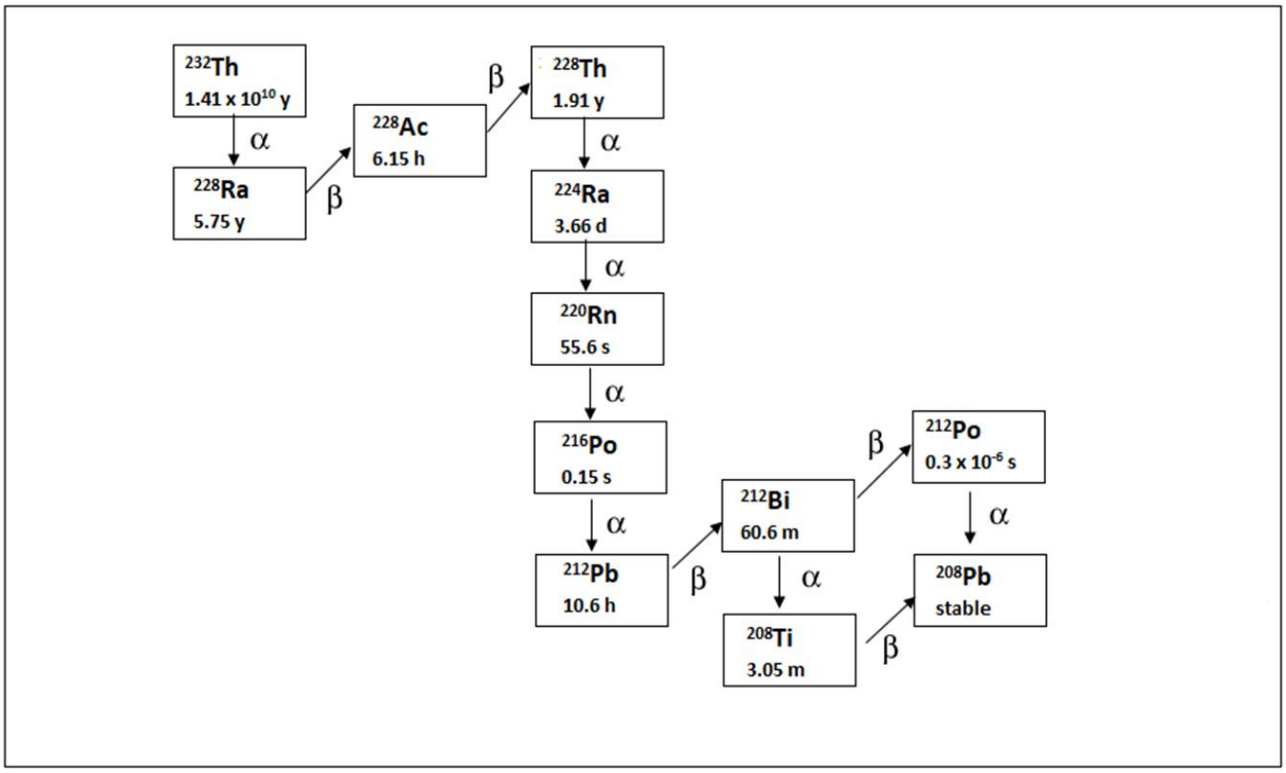


Figure 2: Decay chain of ^{232}Th (Costa *et al*., 2015)

2.2 Radiometric methods and analytical techniques

The use of radiochemical analyses for monitoring radioisotopes in routine laboratories is increasing. Radiochemical methods can detect radioisotopes at trace concentrations. These methods consist of a variety of applications such as radiometric counting methods (including beta (β)-counting, alpha (α)-spectrometry and gamma (γ)-spectrometry). Radiation decay rates are measured with these methods, and the half-life is used to calculate the atom number of the radioisotopes (Hou and Roos, 2008). Liquid scintillation counting (LSC) is also a radiometric technique for determining radioisotopes such as uranium. Using this method, one can measure both alpha and beta decay particles simultaneously. However, as a result of poor detection limits and low energy resolution, this method has problems estimating specific uranium isotopes (Tosheva *et al*., 2004).

Radiometric methods are more sensitive to short-lived radioisotopes whereas mass spectrometric methods are sensitive to long-lived radioisotopes. The main disadvantage of radiometric methods is the long counting and analysis times. This is caused by the long chemical separation process to separate the radioisotopes of interest from the interfering radioisotopes and matrix. As a result, these methods have a low analytical capacity (Hou and Roos, 2008).

Different analytical techniques are used for the analysis of radioisotopes at trace concentrations. Mass spectrometric instruments such as inductively coupled plasma mass spectrometry (ICP-MS) (Aydin and Soylak, 2010; van Es *et al*., 2017), resonance ionization mass spectrometry (RIMS), accelerator mass spectrometry (AMS), thermal ionization mass spectrometry (TIMS) (Trautmann *et al*., 2004), secondary ion mass spectrometry (SIMS) (Tamborini, 2004) and glow discharge mass spectrometry (GDMS) (Hou *et al*., 2005; Valković, 2000) can be used for the analysis of elemental isotopes and radioisotopes (Hou and Roos, 2008). When using these instruments, the atomic numbers of radioisotopes can be measured. These techniques may provide good efficiency and high isobaric suppression. However, these techniques have disadvantages such as background problems and insufficient selectivity (Trautmann *et al*., 2004).

Solid-state mass spectrometric methods with multi-elemental capability: such as laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) (Strashnov *et al*., 2019), GDMS (Hou *et al*., 2005; Valković, 2000) and SIMS (Tamborini, 2004) can analyse long-lived radioisotopes and trace elements directly in solid samples without involving chemical separation. Solid-state mass spectrometry has the advantage of minimizing sample preparation steps, which reduces sample contamination during the preparation process. The disadvantage is that it is difficult to quantify analytical results without appropriate standards and reference materials (Pickhardt *et al*., 2005). In addition, the direct analysis of solid samples is limited for some radioisotopes because their detection limits are too low. Therefore, in order to increase the signal strength and minimize interferences, elements of interest are separated chemically from the matrix (Tamborini, 2004; Limbeck *et al*., 2015).

TIMS has been used as an analytical technique for the determination of radioisotopes and ratio measurements for many decades. However, ICP-MS shows more efficiency compared to TIMS, because of its short sample analysis time and lower costs. ICP-MS also requires smaller sample sizes and reduces the time-consuming chemical separation procedures (Schaumlöffel *et al*., 2005). Because of the greater difficulty in sample preparation and measurement methodologies, TIMS is less preferred than ICP-MS. Many radioisotopes have recently been determined using ICP-MS including ^{99}Tc, ^{226}Ra, ^{235}U, ^{236}U, ^{238}U, ^{232}Th, ^{239}Pu and ^{240}Pu, based on their masses and not on their radioactive properties (Lariviere *et al*., 2005).

ICP-MS has been widely used for the analysis of radioisotopes in environmental samples. ICP-MS is among the most suitable methods for routine analysis of isotopes of uranium, thorium, and other radioisotopes, as well as their ratios. However, due to low concentrations of radioisotopes, the measurements cannot be achieved easily by ICP-MS without proper sample preparation (Aydin and Soylak, 2010; van Es *et al*., 2017). Hence, it is still difficult to directly analyse radioisotopes in geological and environmental samples by ICP-MS because they have low concentrations, and complex matrixes. Different sample preparation methods such as sample dissolution, extraction chromatography are required to extract these radioisotopes.

At present, ICP-MS is the most commonly used mass spectrometric technique for measuring isotope ratios at very low levels, as well as for analysis of radioactive materials at low concentration levels. ICP-MS can be applied to aqueous radioactive solutions and to solid samples after complete dissolution or digestion. The major advantage of ICP-MS over conventional inorganic solid mass spectrometry techniques is the possibility of simple sample introduction and a quick and straightforward quantification process using aqueous standard solutions. Based on interferences and the instrument's sensitivity, ICP-MS limit of detection were 10^{-14} gg^{-1} for U and Th (Nisi *et al*., 2017). In radioisotope determination by ICP-MS, the major uncertainty is the appearance of polyatomic interferences and isobaric interferences caused by other elements with the same mass. ICP-MS with a double-focusing sector field can minimise the polyatomic in the collision reaction cell. In this cell, analyte ions and the cell's gas can collide and cause some signal loss which can reduce the sensitivity. In ICP-QMS using an appropriate reaction gas in a collision/reaction cell can effectively suppress the interfering isobaric ions (van Es *et al*., 2017).

Previous research has looked at naturally occurring ^{234}U, ^{235}U, and ^{238}U as well as artificially produced ^{234}U, ^{235}U, and ^{238}U. However, the evidence for identifying the source of anthropogenic U from ^{235}U and ^{238}U is weak, especially in soil samples. Even when spectrometric techniques such as ICP-MS, AMS and TIMS are commonly used to quantify these radioisotopes of Uranium, the source cannot be identified (Yang *et al*., 2016).

Previous studies by Tuovinen *et al*., (2015) determined the concentration of uranium and thorium isotopes using four different techniques: gamma spectrometry, alpha spectrometry, ICP-MS, and a portable X-ray fluorescence (XRF) spectrometer. Gamma spectrometry and alpha spectrometry which offer low detection limits ranging from 1 mBq for uranium and 0.070 Bq kg^{-1} for thorium, are suitable techniques for determining the radioisotopes activity concentrations in environmental samples. However, mass spectrometers are increasingly used to analyse trace elements. This method is precise, fast, and sensitive with detection limits of µBq and nBq for U and Th (Murphy and Morrison, 2006). A mass of 0.1 to 0.5 g of sample was prepared by microwave digestion using different concentrated acids. Their results showed that the digestion of the sample was best achieved at 20 mL concentrated nitric acid with a sample mass of 0.5 g for extraction of both U and Th. The results for U and Th concentrations were in good agreement for the three techniques, though U concentrations were slightly higher for ICP-MS. Another technique used was a non-destructive, portable X-ray fluorescence (XRF) spectrometer for the determination of thorium (without sample pre-treatment) which also gave comparable results to other methods in their study.

Ndung'u *et al*., (2004) determined the concentration of ^{208}Pb in different types of vinegars by ICP-MS and graphite furnace atomic absorption spectrometry (GFAAS). Samples were prepared by different sample digestions, using nitric acid, hydrogen peroxide and a heating block. A mass of 0.5 to 1 g was weighed into a Teflon container and samples were digested for 2 to 3 hours until dryness was achieved. ICP-MS and GFAAS were used to analyse the digest dissolved in nitric acid and for monitoring radioisotopes. As part of the sample degradation process, hydrogen peroxide was added to the samples. The digestion method gave reproducible lead results for both ICP-MS and GFAAS which ranged from 60 to 319 ppb.

Further studies by Mas *et al*., (2012) determined trace element concentrations and radioisotope ratios of (^{206}Pb, ^{207}Pb, ^{208}Pb, ^{230}Th, ^{232}Th and ^{234}U, ^{238}U) Pb, U and Th using ICP-QMS from the same aliquot. Acid digestion was performed following a U.S. EPA 3050B method (Epa, U.S, 1996). Lead isotope ratios were analysed by ICP-QMS. From the same aliquot U and Th were separated in an Eichrom UTEVA column prior to analysis. A good correlation among Pb isotope ratios $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ was found to be ($r = 0.9762$) for sediment samples. However, the recoveries of U and Th were 90% and 75% respectively. From the same sediment samples, U isotope ratios were found to be in good agreement with those found by Bolivar *et al*. (2002) and Villa *et al*. (2011) whereas $^{232}Th/^{230}Th$ isotope ratios were lower than those found by Bolivar *et al*., (2002).

Recent studies by Mas *et al*., (2020) determined the U and Th isotopes by using microwave digestion followed by evaporation to dryness of sample and analysis using ICP-MS. This method proved to yield accurate and repeatable results. The purification step of using TEVA and Uteva resin for separation showed to decrease the concentrations of Th and U in the sample. The digestion method was applied to certified reference sample IAEA-385 and IAG DBC-1 for the determination of isotope ratios ($^{238}U/^{235}U$, $^{238}U/^{234}U$, $^{232}Th/^{230}Th$) and the concentrations of U and Th (from the isotope ratios $^{238}U/^{236}U$ and ^{232}Th /^{229}Th, respectively). Based on the accuracy and reproducibility performances, the proposed methodology provided satisfactory results. For the two aliquots analyzed, the activity ratios were 0.004632 ± 0.00026 and 0.004638 ± 0.00015 for $^{235}U/^{238}U$, 1.031 ± 0.016 and 1.042 ± 0.010 for $^{234}U/^{238}U$, and 1.033 ± 0.040 and 1.080 ± 0.027 and for $^{230}Th/^{232}Th$, respectively.

2.3 Separation methods

Samples with significant matrix effect requires purification before analysis. Extraction resins or anion exchange resins are well known for separating radioisotopes and actinides from the matrix in environmental samples (Acikara, 2013). Ion exchange chromatography is one of the most widely used techniques for separating and isolating metals due to its high degree of selectivity, reversibility, brief separation times, and other advantages. For the separation of uranium and thorium, anion-exchange resins have been extensively used. Trans Uranian (TRU), Tetravalent Actinides (TEVA), Uranium and Tetravalent Actinides (UTEVA), DGA and Dowex (AmberChrom) resins have previously been used to successfully separate and purify radioisotopes and actinides.

Separation methods utilizing TEVA, U/TEVA, and TRU resins have become popular for the separation of U and Th in environmental samples. These resins can also be used to separate other radioisotopes like americium and plutonium to obtain their radio activities. Employing these resins allows for easier and faster separations of radioisotopes than previous approaches, such as precipitation techniques, liquid–liquid extractions and the use of alpha spectrometry which is time consuming due to long-time radiation counting.

Total U and $^{235}U/^{238}U$ isotope ratio measurements in freshwater samples were studied utilizing TRU resin cartridges for separation of minor and major elements and a quadrupole ICP-MS was used for the analysis (Tagami and Uchida, 2007). Three alkaline reagents, tetra-methyl ammonium hydroxide (TMAH), NaOH, and NH_4OH, were investigated for U elution behaviour from the TRU resin cartridges. TMAH produced the best results among the eluents investigated, with a high U recovery with less

interferences. From the elution process Th and REE's was eluted using 20 mL of 0.5 M HCl (at a flow rate of 4 mL per minute) (Tagami and Uchida, 2007).

Normal type DGA resin (N, N, N', N'-tetra-n-octyldiglycolamide as the extractant system) is another promising resin for U purification among the current extraction chromatographic resins. It has been used by Yang *et al*. (2016) to separate uranium isotopes especially ^{236}U from other matrix elements. Their study compared normal dissolution (acid leaching) and whole dissolution (full digestion) methodologies for measuring U atom ratios in environmental materials. During the DGA resin purification technique, almost no loss of U was observed. The established method was tested initially on four soil and sediment reference materials before being used to analyze contaminated soil samples. The procedures for total dissolution (an acid mixture of HF, HNO_3, and $HClO_4$) and acid leaching (8 M HNO_3 or concentrated HNO_3) were evaluated as acid attack methods for dissolving U. The results obtained utilizing the acid leaching process and the total dissolution procedure for u isotopes differed. The concentrated HNO_3 was found to be a better acid for complete U isotope recovery in the current study for acid leaching. To summarize, the total dissolving technique used in this investigation was effective in releasing U isotopes from environmental samples.

Monroy Guzmán (2016) separated uranium from its daughter radioisotopes using Dowex 1X8 20-50 mesh and Amberlite IRA (100 mesh) resins. The long-lived radioisotopes were eluted and recovered with varying concentrations of HCl solutions (4 M, 8 M) and H_2O. The separated uranium was then quantified using Gamma and alpha spectrometry. The results yielded greater than 99% recovery for uranium and thorium when using Dowex 1X8 20-50 mesh and Dowex 1X8 200 mesh, but other radioisotopes yielded slightly lower results due to their adsorption properties to the resin caused by the eluent used. Amberlite IRA (100 mesh) resin also yielded greater than 99% recovery for uranium. 95% recovery for thorium was also achieved with this resin but for other radioisotopes such as radium the recovery was less than 70%.

The adsorption properties of U and Th radioisotopes including Ra, Pa, Pb, Bi, and Po in HCl medium in an anion exchange resin was also reported, where Th was not adsorbed in HCl medium. U was weakly adsorbed at < 1 M HCl medium and adsorbed more at > 1 M HCl medium and was recovered with H_2O or diluted HCl solution. Radioisotopes such a Ra and Pa were eluted at 4 M HCl, Pb at 8 M HCl and there was no recovery of Bi and Po (Monroy Guzmán, 2016).

An anion-exchange column was used by Juntunen *et al*., (2001) to separate uranium, thorium, and radium from rock samples. The acid dissolved samples were added to an anion-exchange column that has already been pre-treated with 9 M HCl. From the resin thorium and radium, which do not adsorb to the resin or form chloride complexes, eluted through the column, while the uranium retained on the column since it forms uranium chloride complex. With the breakdown of the uranium chloride complexes, uranium was eluted from the column as a cationic and determined by liquid scintillation spectrometry.

Three chromatography columns were used by Crespo *et al.,* (2001) to achieve the separation of long-lived radioisotopes and actinides (U, Th, Ra, and Pa) from geological samples. With the use of 9 M HCl, thorium and radium were recovered in the eluted solution while the uranium was adsorbed on a Dowex 1X8 200 mesh anion-exchange resin column. The radium that was present in the eluate of the second column was subsequently purified using Dowex 50 WX8 100 mesh, at pH 1, whereas thorium was adsorbed using a separate anion-exchange resin in a solution containing 8 M HNO_3.

A study by Alhassanieh *et al*., (1999) reported the behaviour of Th, U, Pa, Ra, and Ac on the DOWEX 1X8 resin using both HNO_3 and HCl medium as eluents. The results showed that thorium was not adsorbed in this resin when using high concentrated HCl medium but was adsorbed at high concentrated HNO_3 medium. Uranium also retains in the resin at high concentrated HCL medium whereas at high concentrated HNO_3 medium it does not show any adsorption towards the resin. It was also found that all HNO_3 and HCl concentrations result in the adsorption of thorium onto the cation exchange resin DOWEX 50 WX8. Uranium was also adsorbed on the DOWEX 50 WX8 resin (cation exchange resin) in high concentrations of HNO_3 and HCl. It was also adsorbed on the DOWEX 1X8 resin (anion exchange resin) at low concentrations of HNO_3 and HCl when used as a medium.

CHAPTER 3: STUDY OBJECTIVES

3.1 General objective

The aim of this project was to determine the long-lived radioisotopes of U and Th in soil and mine tailings samples by ICP-QMS after acid digestion followed by separation and preconcentration using anion AmberChrom resins.

3.2 Specific objectives

The specific objectives are as follows:

- To develop suitable sample preparation method for the soil (radioisotopes reference materials) and mine tailings solid samples using hot plate and microwave acid digestion.
- To optimise and microwave digestion method by varying the sample mass (0.2 to 0.5g), extraction time (1 to 2.5 hrs), and difference concentrations of the acids.
- To optimise the hot plate digestion method by varying the sample mass (0.2 to 0.5g), extraction time (1 to 2.5 hrs), and difference acid volumes.
- To separate and preconcentrate U and Th radioisotopes using AmberChrom (Dowex) resins from the digested samples.
- To quantify the digested, extracted and preconcentrated certified reference materials and the mine tailing samples using ICP-QMS.

3.3 Motivation for the study

Radioisotopes are a source for contamination to the environment as they are brought to the surface as waste disposal from mines, fuel enrichment, waste storage etc. These radioisotopes become exposed to weathering and leaching with water which led to them undergoing a decay process. The decay products of the U and Th series are toxic and high exposure may lead to health risks if not monitored. This enhances the natural radiation which may lead to elevated radiation exposure to people living near these contaminated environments. Radioisotopes analysis is therefore required for environmental remediation, decontamination, and monitoring. Very few methods have been developed for the analysis of these U and Th radioisotopes especially from a South African perspective. Most analytical methods are from developed countries. ICP-QMS is a technique that can be used to quantify these radioisotopes. Hence the study aims to determine the radioisotopes of U and Th.

3.4 Hypothesis and research questions

3.4.1 Hypothesis

The target radioisotopes of U and Th can be analysed by ICP-QMS after acid digestion followed by separation and preconcentration using AmberChrom (Dowex) resins.

3.4.2 Research questions

The study aims to answer the following question:

- Is it possible to quantitatively extract U and Th radioisotopes from solid CRMS and solid mine tailings samples using hot plate or microwave digestion?
- Is it possible to isolate and concentrate U and Th isotopes extracted from hot plate acid digestion using anion resins?

CHAPTER 4: MATERIALS AND METHODS

4.1 Sample collection

The two soil certified reference materials GXR6 and OREAS45e containing the radioisotopes of interest, U and Th were selected and purchased based on the availability from the Laboratory of the Government Chemist (LGC) Ltd (Midrand, South Africa) and OREAS (Bayswater North, Australia). The two samples used in this study are mine tailing samples. The samples are described as ERGO carbon-in-leach (CIL) concentration residue which contains cyanide for sample 1(483) and sample 2(488) was described as a Harmony feed from the plant. The samples were obtained from the Hydrometallurgy department at Mintek. They were chosen as they contained both U and Th and due to the availability.

4.2 Chemicals and reagents

Analytical grade HNO_3 (65%), $HClO_4$ (70%) and H_2O_2 (50%) were purchased from Associated Chemical Enterprises (ACE) PTY LTD (Johannesburg, South Africa). HF (48%) and HCl (37%) were purchased from Merck (Pty) Ltd (Modderfontein, South Africa). Milli-Q water (18.2 MΩ × cm (million Ohms)) was used to prepare all the samples and solutions used in this study. The resins AmberChrom 1x2 50-100 mesh, AmberChrom 1x8 20-50 mesh and AmberChrom 1x8 50-100 mesh were purchased from Merck (Pty) Ltd (Modderfontein, South Africa). The internal standards, indium and rhenium were used. Indium (10000 and 1000 µg/mL) in 5% HNO_3 was purchased from De Bruyn spectroscopic solutions (Midrand, South Africa). Rhenium (10000 and 1000 µg/mL) in 5% HNO_3 was purchased from Stargate Scientific (Johannesburg, South Africa). These internal standards were used to investigate the recoveries of the analytical procedure. Uranium and Thorium standards (10000 and 1000 µg/mL) in 5% HNO_3 were purchased from Laboratory of the Government Chemist (LGC) Ltd (Johannesburg, South Africa. A multi element standard (5 and 100 µg/mL) in 5% HNO_3 were purchased from De Bruyn spectroscopic solutions (Midrand, South Africa). The United States Geological Survey Geo-Chemical Exploration Standard Reference Materials GXR-6 was purchased from LGC Ltd (Johannesburg, South Africa) and was used as the certified reference material. Another CRM which was used is OREAS 45e which was purchased from OREAS (Bayswater North, Australia).

The eluents used for the separation step in this study were prepared by diluting the analytical grade HCl (37%) to make the 1 M, 2 M, 3 M, 4 M, and 8 M HCl solutions with Milli-Q water. The prepared solutions were also used to precondition the column resins as well as to elute the U and Th from the loaded sample in the column. A 2% rinse solution was also prepared by diluting HNO_3 (65%), and it was used in the rinse station during sample analysis.

4.3 Apparatus and Instrumentation

- A Thermo Scientific™ iCAP™ Q ICP-MS (ICP-QMS). The ICP-QMS coupled with a quadrupole was used to quantify the acid digested samples as well as the separated and concentrated samples from the AmberChrom resins. Table of instrument conditions is attached in appendix EE.
- Microwave digestion system (Mars 6 CEM) - This instrument was used for sample acid digestion at a controlled temperature and pressure. The temperature set was 800 W and the overall sample digestion was 90 minutes.
- Hot plate (EcoPlate) – The EcoPlate was used for sample acid digestion at a temperature between 100 to 160 °C under a fume hood. The model code is 502, with power rating at 230V (W) of 3000 and temperature range up to 250˚C.

4.4 Quality Assurance

Calibration standard solutions and internal standard solutions were prepared from multi element standard (5 and 100 µg/mL) in 5% HNO_3, U and Th standard solution (10000 and 1000 µg/mL) in 5% HNO_3. A range of standards (5, 10, 20, 40, 60 and 100 ppb) were prepared from the stock solutions and were transferred into appropriately sized volumetric flasks (50 mL) by means of dilution. Standard solutions were diluted and filled to the mark using Milli-Q water obtained from the Milli-Q purifier tank. Samples and reagents were acidified using analytical grade HNO_3 (2%). All test work including storage of reagents was performed under room temperature.

The homogenised soil CRMs (GXR-6 and OREAS 45e) and mine tailings Samples (Sample 1(483) and sample 2(488)) were prepared in triplicates with each set of samples having a blank. These CRMs were used evaluate the sample preparation procedure in order to determine the method's accuracy, precision, and repeatability. Internal standards (In and Re) were used to monitor the methods recovery for the analysed CRMs, samples, and blanks. A rinse solution was also prepared, and it was run before and after each sample analysis. Sample blanks were also analysed before and after each set of replicates to monitor if there are U and Th radioisotopes present in the reagents. Blanks were also used

as extra rinse to prevent cross contamination from the previous analysed sample batch to the next batch. All samples were analysed on a cleaned and calibrated instrument.

4.5 Cleaning protocol

All glassware and Teflon's used for digestion were cleaned with liquid laboratory grade detergent, deionized water, and Milli-Q water. The glassware was then rinsed with water and 10% (v/v) HNO_3 followed by thoroughly rinsing with Milli-Q water and were allowed to dry before sample preparation. The cleaning process was adhered to minimize the risk of contamination to the samples and standards.

4.6 Methodology

4.6.1 Solid sample preparation

4.6.1.1 Method 1: Hot plate acid digestion

A combination of the following acids HNO_3, HCl, HF, $HClO_4$ and H_2O_2 were used to digest the samples. A mass between 0.2 to 0.5 g of soil or tailing samples was weighed in triplicate into Teflon beakers (polytetrafluoroethylene (PTFE)) and a few drops of Milli-Q water were added to the Teflon beakers to prevent the samples from scattering on the Teflon. A total volume of 20 mL of the four different acid combinations (HNO_3, HCl, HF and H_2O_2) was added into the Teflon beakers with weighed samples for test 1(refer to Chapter 5, table 2). A total volume of 30 to 35 mL of the four acid combinations (HNO_3, HF, $HClO_4$ and H_2O_2) was added into the Teflon beakers with weighed samples for test 3. The samples were then digested on the hot plate until dryness at a temperature between 100 to 160 °C under a fume hood. Teflon beakers were removed from the hot plate and the samples were allowed to cool. After cooling, 10 mL of HNO_3 and a few drops of H_2O_2 were added to reconstitute the samples and- to redissolve the residue. The samples were digested again on a hot plate for less than 10 minutes and then they were allowed to cool. The samples were then transferred into a 50 mL volumetric flask and filled up to the mark with Milli-Q water and the solution was thoroughly mixed by shaking. All the samples were allowed to settle in order to separate any residues from the solution before analysis by ICP-QMS.

4.6.1.2 Method 2: Microwave digestion.

Masses of soil and tailing samples between 0.2 and 0.5 g were weighed in triplicate into Teflon vessel and few drops of Milli-Q water were added. A total of 30 mL acid combinations of HNO_3, HF, and $HClO_4$ (3:2:1) were added to the Teflon vessels (polytetrafluoroethylene (PTFE)). The Teflon vessels were

closed with lids and loaded on the MARSXpress Plus vessel. The samples were digested on the microwave at a temperature of 220°C. The digestion program for microwave was started with a two-step ramp until 220°C was reached. The microwave parameters are represented in Table 1. After the digestion was completed, the vessels were kept tightly closed until a temperature of less than 20°C was attained. The vessels were removed at room temperature. The caps were removed and rinsed with Milli-Q water. The solutions were transferred into clean Teflon beakers and the walls and bottom of the vessel's liners were thoroughly rinsed with Milli-Q water. The resulting volume solution in mL was evaporated to incipient dryness on a hot plate. The samples were then allowed to cool and were reconstituted with 10 mL of HNO_3 and a few drops of H_2O_2. The samples were digested again for less than 10 minutes and then they were allowed to cool. The samples were then transferred into a 50 mL volumetric flask and filled up to the mark with Milli-Q water and the solution was thoroughly mixed by shaking. All the samples were allowed to settle in order to separate any residues from the solution before analysis by ICP-QMS.

Table 1: Optimum optimization of microwave digestion parameters

Step	Power (W)	Ramp time (minutes)	Temperature (°C)	Hold time (minutes)
1	800	5	100	15
2	800	15	220	40

4.7 Separation and Preconcentration of U and Th on AmberChrom resins

Three anion resins were chosen for this study to conduct the separation and preconcentration of U and Th from the hot plate acid digested CRMs and mine tailings samples. Different sizes of strong base, spherical fine mesh AmberChrom ion exchange resins were used to separate the U and Th from the CRMs samples. These anion resins are known as Dowex or AmberChrom with the molecular formula [$C_{29}H_{34}ClN$] and IUPAC name 1,4-bis(ethenyl)benzene;(4-ethenylphenyl)-trimethylazanium; styrene; chloride. The three resins namely AmberChrom 1x2 50-100 mesh, AmberChrom 1x8 20-50 mesh and AmberChrom 1x8 50-100 mesh were evaluated for the effective separations of U and Th from the acid digested CRMs and mine tailings samples. The X number on the resin describes the degree of resin cross-linkage which is the percentage of the divinylbenzene (DVB) in the resin copolymer. AmberChrom 1x8 20-50 mesh for example is a type 1 strong base anion resin containing 8% DVB whereas AmberChrom 1x2 50-100 mesh contains 2% DVB.

4.8 Preparation of separation and preconcentration eluents

The eluents used were different molarities of HCl (1 M, 2 M, 3 M, 4 M, and 8 M) and Milli-Q water. The HCl solvents were prepared into 500 mL volumetric flasks by diluting the analytical grade HCl (37%) with Milli-Q water. The eluents were used to separate and preconcentrate U and Th from the column resin. The value of molarity for HCl (12.1 M) was calculated using the specific gravity formula. The 12.1 M HCl was applied to formula 1 to calculate different HCl concentrations. Where C is the concentration in mol/L (M) and V is the volume in litres (L). The number 1 represents the initial for both concentration and volume and the number 2 represent the final for both volume and concentration.

Formula 1: $C1 \times V1 = C2 \times V2$

4.8.1 Column set up and packing

A 50 mL reservoir chromatography glass column shown in Figure 3 was used for the separation of radioisotopes. The column was packed with the anion resins AmberChrom 1x2 50-100 mesh, AmberChrom 1x8 20-50 mesh and AmberChrom 1x8 50-100 mesh for each separation. Milli-Q water was used as the mobile phase and was also used to do the wet packing (slurry packing) of the resins into the columns. The column was secured into a vertical stand by clamping it upright. Resin slurry was prepared in a 50 mL volumetric flask and air bubbles were eliminated by gentle tapping the flask. The 50 mL resin slurry was transferred into the column using a funnel and the column inner walls were rinsed with Milli-Q water.

The packed resins were allowed to settle and any air bubble formation inside the column were eliminated by tapping the column with a rubber tube to re-level and promote a uniform density in the column. After the resins had settled a cotton wool was inserted on top of the resin bed to prevent the resin bed layer from being disturbed during sample and eluent introduction. The packed column resin was maintained hydrated by addition of eluents to prevent the resins from drying out.

An air pump was connected to the column with a tubing, to control the flow rate of the sample and eluent. The eluates flow rate was also controlled by adjusting the stopcock. In addition, syringes were also used for sample introduction.

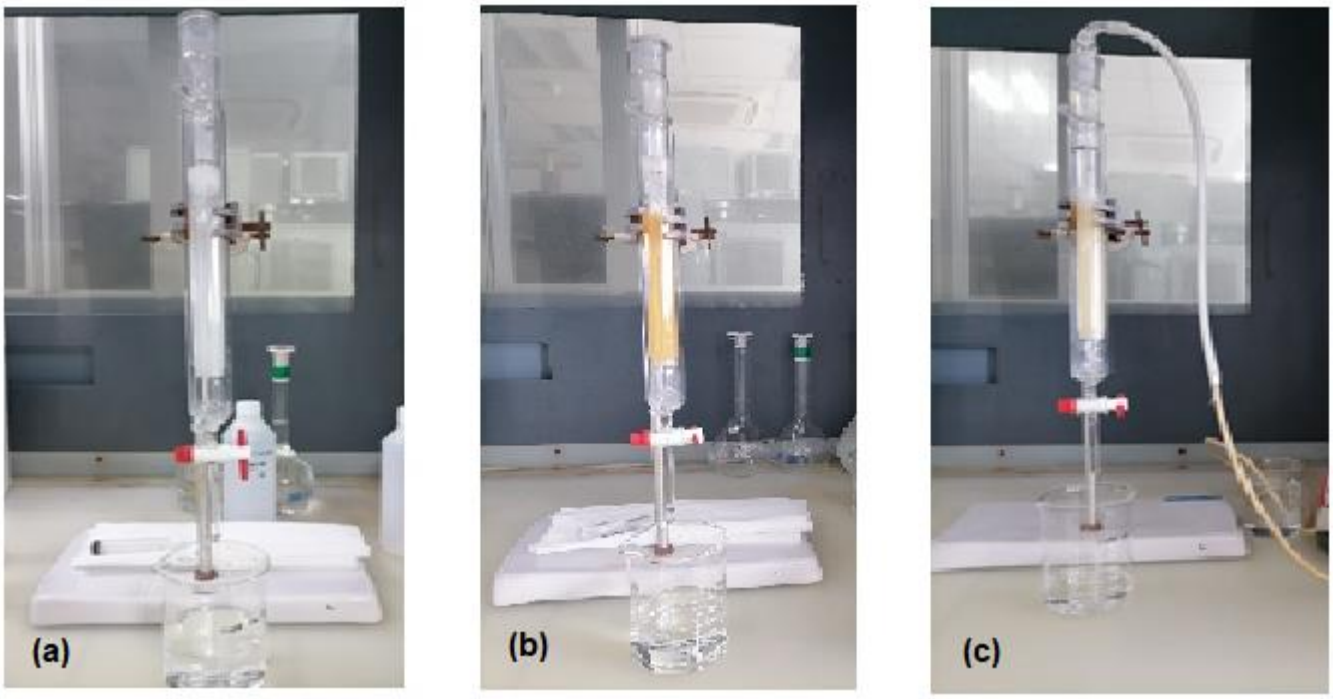


Figure 3: Diagram of column setup packed with AmberChrom resins. (a) AmberChrom 1x2 50-100 mesh; (b) AmberChrom 1x8 20-50 mesh; (c) AmberChrom 1x8 50-100 mesh.

4.9 Resins preconditioning

4.9.1 Preconditioning of resins using HCl solutions and Milli-Q water

The packed ion exchange resins AmberChrom 1x2 50-100 mesh, AmberChrom 1x8 20-50 mesh and AmberChrom 1x8 50-100 mesh were preconditioned by following a four-step sequence. Various HCl solvents (1 M, 2 M, 3 M, 4 M, and 8 M HCl) and Milli- Q water were used to precondition the column resin before the CRMs and samples were introduced. The column resin was first rinsed with 100 mL of Milli-Q water, followed by 100 mL of 8 M HCl, and lastly by another 100 mL of Milli-Q water. After these steps 100 mL of the selected HCl solvent for that specific separation was introduced into the column to activate the resins before the samples were introduced.

For safety reasons, no HNO_3 solvents were used in this study to perform separations on the resin column. Solutions such as bleach, chlorine-generating solutions, nitric acid, chromic acid solutions, as well as peroxide, were all avoided as per Dowex guidelines. The use of strong oxidizing agents such as HNO_3 acid causes fast oxidation upon contact with resins. This can result in a potentially explosive reaction under the wrong circumstances.

4.10 Separation and preconcentration steps

After preconditioning the column resin, 20 mL of the digested sample volume was added into the column resin using a pump or a syringe and a 10-minute contact time of the sample with the resin was implemented before the sample was eluted. 100 mL of the selected HCl solvent (e.g., 4 M HCl or 8 M HCl) was gradually introduced into the column resins, while the eluent was being added the stopcock was subsequently opened to start the elution process. The eluates were collected into vials in different fractions without allowing the resin to dry up. The eluates from the HCl eluent were collected into vial 1 to vial 12. The volume of the eluates collected in each vial depended on the colour of the eluate, 10 mL was collected for clear solutions and 5 mL was collected for the yellow eluents. After the collection of eluate into vial 12, the eluent was changed to Milli-Q water. 100 mL of Milli-Q water was also gradually introduced into the column resin to elute the remaining adsorbed sample. The eluates from the Milli-Q water were collected into vial 13 to vial 24.

4.11 Resin separation and preconcentration optimisation

The separation process was conducted using the parameters mentioned in this section. The elution process was carried out at a flow rate of 2 to 3 BV/hr (1.67 to2.50 mL /minutes). The eluates were collected into a set of 12 test tubes or vials for each eluent used, in fractions of 10 mL for the first vial, 5 mL for the yellow-coloured bands and 8 mL for the rest of the fractions. In overall 24 test tubes or vials were used to collect the eluates. Vial 1 to 12 contained the sample eluates from concentrated HCl eluent and vial 13 to 24 contained eluates from Milli-Q water.

4.11.1 Effect of the loaded sample volume

Different volumes of the hot plate acid digested samples (10 mL, 15 mL, 18 mL, and 20 mL) were loaded onto the column resin to evaluate the effect of the sample volume loaded on the column resin. The samples were pumped and loaded into the preconditioned column resin and were allowed to adsorb and react with the resin for 10 minutes before the elution process was carried out. The elution process was carried out using 100 mL of 4 M HCl and Milli-Q water separately.

4.11.2 Effect of the concentration of HCl elution solvent

The effect of HCl elution solvents was evaluated in the column resin to determine which HCl solvent concentration produces better separation and preconcentration results of U and Th from the hot plate digested samples. The HCl elution solvents tested were 1 M, 2 M, 3 M, 4 M, and 8 M HCl. This

procedure was carried out using a 20 mL acid digested sample and 100 mL of each of HCl eluents and Milli-Q water.

4.11.3 Effect of sample contact time

The hot plate acid digested samples were tested for the effect of contact time (< 1, 10 and 20 minutes) after loading on the column resin. This was done to determine the effective contact time for full sample adsorption and reaction with the resins. The loaded 20 mL sample was allowed to adsorb and react with the resins for a certain period and then it was eluted using 100 mL of 4 M HCl solution and Milli-Q water.

4.11.4 Effect of the sample's eluate pH

The pH of the eluates was evaluated and recorded for the collected fractions after separation and preconcentration. However, the pH for 8 M HCl eluates was not recorded since it is highly acidic and has a negative pH.

4.12 Summary of column parameters on sample separation and preconcentration

- Column used and size: Chromatography glass column 50 mL reservoir.
- Resins: AmberChrom 1x2 50-100 mesh, AmberChrom 1x8 20-50 mesh and AmberChrom 1x8 50-100 mesh
- Eluent used: 100 mL each of (1 M, 2 M, 3 M, 4 M, and 8 M) HCl and Milli-Q water.
- Flow rate: A flow rate of 2 to 3 BV/ hr (1.67 – 2.50 mL /minutes)
- Sample contact time: < 1, 10 and 20 minutes
- Sample loading: 10 mL, 15 mL, 18 mL, and 20 mL
- Detector used: Thermo Scientific™ iCAP™ Q ICP-MS (ICP-QMS)

4.13 Sample analysis

4.13.1 Quadrupole inductively coupled plasma mass spectrometry (ICP-QMS)

The analyses of standards, the hot plate acid digests and the separated and preconcentrated GXR-6, OREAS 45e, Sample 1(483) and Sample 2(488) was performed using the Thermo Scientific™ iCAP™ Q ICP-MS (ICP-QMS). The method used for the analysis was optimised with the prepared standard calibration solutions, internal standards and by using different analysis modes (standard and kinetic energy discrimination). The calibration standard solutions were diluted using an auto dilutor prior to

analysis to also incorporate the addition of the internal standards (Indium and Rhenium). The hot plate acid digested samples and CRMs were also diluted using an auto dilutor before analysis on ICP-QMS. A full schematic diagram with and overview of the CRMs and sample preparations until the sample analysis on the ICP-QMS is provided in Figure 4.

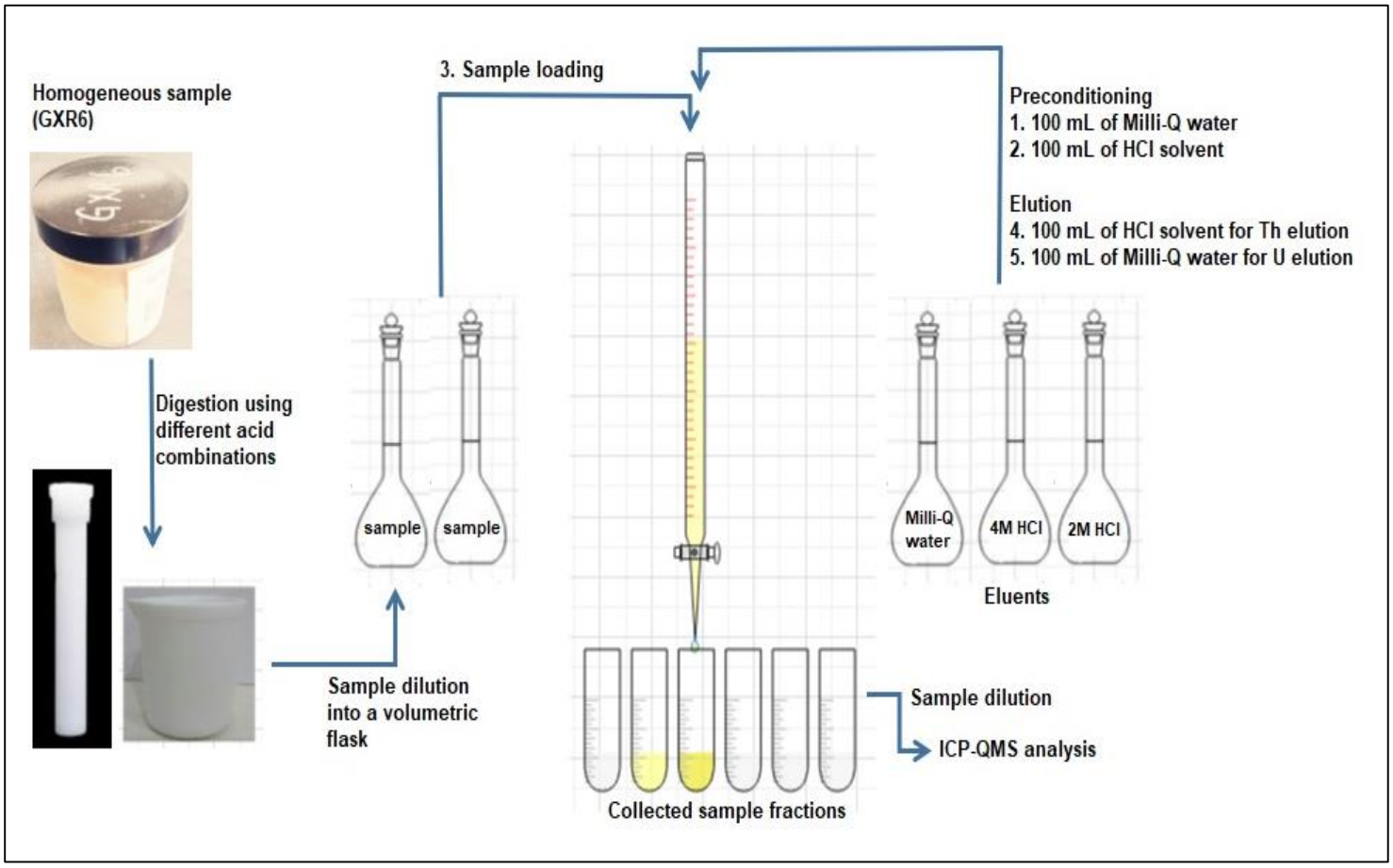


Figure 4: Schematic diagram of an overview of the sample digestion methods, column separation, preconcentration and analysis by ICP-QMS.

4.14 Optimization of the instruments

During instrument optimization, the Thermo Scientific™ iCAP™ Q ICP-MS (ICP-QMS) instrument allows for a choice in the gas mode which can be utilized during the analysis of samples. These gas modes are kinetic energy discrimination (KED) which uses of Helium (He) gas during sample analysis and the standard (STD) mode which uses Argon (Ar) gas during analysis on the ICP-QMS.

The advantages of using helium as collision gas are that it does not react with the sample matrix because it is inert, multiple interferences from the same analyte can be removed and that there is no need to use interference correction equations to remove the interferences. The samples were analysed

using both gas modes (KED and STD) in order to optimize the method. CRM GXR-6 which contains radioisotopes elements as well as base metals elements was evaluated for the two gas modes and the results were compared as to which gas mode yielded better results.

4.15 Standards and Standard Curve

Multiple standards were prepared from external and internal standards to measure the radioisotopes from the GXR-6 and environmental samples using ICP-QMS. The standards were prepared to quantify both liquid and solid samples. The internal and external standards were prepared by diluting the stock solutions to the desired concentrations needed to analyse the samples. Further dilutions were carried out which included the addition of internal standards to the standards prepared. The standards ranged from 5 ppb to 100 ppb.

4.16 Preparation of stock solution

The stock solutions were prepared from the uranium, thorium and the multi standard solutions to a concentration of 1 ppm, using calibrated micropipettes. The prepared stock solutions were stored at room temperature. From the stock solutions, a set of working solutions were prepared regularly through a series of dilutions and were used as calibration standard solutions before each analysis. All the calibration standards were prepared using a calibrated auto dilutor.

CHAPTER 5: RESULTS AND DISCUSSION

This chapter is made of two sections, section 5.1 which discusses the results of method optimisation and section 5.2 which discusses the results of the application of the optimised methods. The results for U and Th are reported from the most abundant radioisotopes ^{238}U and ^{232}Th.

The overall percent recoveries for ^{232}Th and ^{238}U were calculated using formula 2.

- Formula 2: Percent recovery = (amount extracted from digestion ÷ amount in the original samples) × 100
- Example: Percent recovery of ^{232}Th = (4.16 ppm / 5.30 ppm) x 100 = 78.46%

5.1 METHOD OPTIMISATION.

5.1.1 Acid digestion optimisation results

The soil CRM GXR-6 containing 1.54 ppm U and 5.30 ppm Th was used to optimise the acid digestion methods. The sample preparation was done based on the multi acid digestion method using various acid combinations of HF, HCl, HNO_3, H_2O_2 and $HClO_4$. The CRM was prepared in triplicate by the hot plate and the microwave acid digestion procedure. Three tests, namely test 1, test 2 and test 3 were conducted during method optimisation and the results are reported in Table 2, Table 3, Table 4, and Table 5. From the three tests, methods with different acid combinations namely method 1, method 2, method 3 and method 4 were used during acid digestion to digest the CRM GXR-6 in order to optimise and achieve the desired certified values of ^{238}U and ^{232}Th radioisotopes. The average results of the digested samples were reported.

5.1.1.1 Hot plate acid digestion optimisation (Test 1)

Test 1 results in Table 2 shows the results of the hot plate acid digestion methods (method 1 to 4), where 20 mL of acid combinations (HCl, HNO_3, HF and H_2O_2) were evaluated for the hot plate acid digestion of the soil CRM GXR-6. The acid combinations were varied according to the four methods presented in Table 2. The recoveries for ^{238}U were greater than 97% in all four methods, whereas the recovery for ^{232}Th was less than 95.85% in all four methods, which is the minimum allowed value for CRM GXR-6. The highest recovery for ^{232}Th was 78.46% which was obtained from method 1 which consisted of high HNO_3 acid volume and low HCl volume. Test 1 methods could extract ^{232}U to its full recovery, however, partially extraction of ^{232}Th was observed. The difference between Th results for

method 1 and 3 could be that the reaction of the acids were not strong enough to carry out the full extraction of Th. The ratio of the acids used for digestion affects the extraction of each element differently.

Table 2: Shows results of test 1 for hot plate acid digestion of GXR-6 using HCl, HNO_3 and HF acid combinations

Test 1	**Methods for Hot plate acid digestion**	**CRM**	**^{232}Th (ppm)**	**% Recovery for ^{232}Th**	**^{238}U (ppm)**	**% Recovery for ^{238}U**
Method 1	16 mL HNO_3 + 3 mL HCl +1 mL HF	GXR-6	4.16	78.46	1.58	102.62
Method 2	3 mL HNO_3 + 16 mL HCl +1 mL HF	GXR-6	2.77	52.24	1.50	97.25
Method 3	15 mL HNO_3 + 4 mL HCl +1 mL HF	GXR-6	2.09	39.37	1.56	101.36
Method 4	10 mL HNO_3 + 5 mL HCl +5 mL HF	GXR-6	3.27	61.66	1.51	97.75

5.1.1.2 Microwave acid digestion optimisation (Test 2)

Table 3 shows the results for test 2 obtained from the microwave acid digestion method. The microwave acid digestion method also yielded greater than 97% recoveries for ^{238}U in all four methods. The highest recovery for ^{232}Th from all four methods was 1.73 ppm (32.62%) which was below the allowed minimum interval of 5.08 ppm. This method was also good for extracting ^{238}U compared to ^{232}Th. The acid combination partially extracted ^{232}Th.When comparing the hot plate acid digestion results (Table 2) and microwave acid digestion results (Table 3), the hot plate acid digestion produced better recoveries in terms of Th than the microwave digestion method. This was caused by the parameters used on the microwave.

In conclusion the microwave acid digestion method was not pursued further since the results were not satisfactory, due to the low recoveries for ^{232}Th. The microwave method was also time consuming compared to the hotplate acid digestion, The method required a second step which included evaporation of HF on the hot plate.

Table 3: Shows results for microwave acid digestion of GXR-6 using different acid combinations

Test 2	Methods for Hot plate acid digestion	CRM	^{232}Th (ppm)	% Recovery for ^{232}Th	% Error for ^{232}Th	^{238}U (ppm)	% Recovery for ^{238}U	% Error for ^{238}U
Method 1	16 mL HNO_3 + 3 mL HCl +1 mL HF	GXR-6	1.16	21.83	78.11	1.58	102.39	2.60
Method 2	3 mL HNO_3 + 16 mL HCl +1 mL HF	GXR-6	0.18	3.34	96.60	1.62	105.10	5.19
Method 3	15 mL HNO_3 + 4 mL HCl +1 mL HF	GXR-6	1.73	32.62	67.36	1.56	101.06	1.30
Method 4	10 mL HNO_3 + 5 mL HCl +5 mL HF	GXR-6	0.05	0.99	99.06	0.34	22.31	77.92

5.1.1.3 Hot plate acid digestion optimisation (Test 3)

The hot plate acid digestion method 1 from Test 1 was optimised further by replacing HCl with $HClO_4$. The total volume of the acid combinations was increased to 30 mL as shown in Table 4 in method 1. The volumes of the acid combinations were then varied from method 2 to 4 by adding extra volume of 5 mL of the acids digested on the methods while the other acids combinations volumes were kept constant. This resulted in the sample being digested by 35 mL of the acid combinations from method 2 to method 4.

The results for the optimisation are reported in Table 4 and Table 5, where Table 4 shows the concentration recoveries of both ^{232}Th and ^{238}U from the applied analysis modes (STD and KED) in ppm. Table 5 shows the percent recoveries of ^{232}Th and ^{238}U results which are reported in Table 4. The results showed better recovery after $HClO_4$ was introduced into the hot plate acid digestion. The radioisotopes of ^{232}Th and ^{238}U were recovered with greater than 98% for all four methods. Method 1 resulted in recoveries which were in the range of 98.58% to 99.80% for both ^{232}Th and ^{238}U. Method 2 to4 resulted in more than 100% recovery for both ^{238}U and ^{232}Th radioisotopes when HNO_3, HF and

$HClO_4$ were increased by 5 mL each. This had a significant effect on the digestion as it improved the recoveries of both ^{232}Th and ^{238}U.

The increase in HNO_3 (method 2) showed greater than 100% recovery for both ^{232}Th and ^{238}U which still lies within the confidence intervals of the certified values of GXR-6 (5.30 ppm ^{232}Th (95.85%-104.15%) and 1.54 ppm ^{238}U (95.45%-104.55%)). The increase in HF (method 3) yielded greater than 100% recovery for both ^{232}Th and ^{238}U. The recovery for ^{238}U were over the GXR-6 highest confidence interval for both the STD and KED mode. The increase in $HClO_4$ (method 4) also yielded greater than 100% recoveries for both ^{232}Th and ^{238}U. The results for ^{232}Th STD, ^{238}U STD and ^{238}U KED mode in this method were outside the confidence interval limits of GXR-6.

From the optimisation results in Table 4 and Table 5, method 1 was chosen as the four-acid digestion combination method to be applied- for the sample preparation by the hot plate acid digestion. Method 2-4 was over extracting ^{238}U and ^{232}Th, hence the method was not applied to the samples.

Table 4: Optimised acid digestion methods using HF+ HNO_3 + $HClO_4$

Test 3	**Acid digestion methods**	**^{232}Th (KED) (ppm)**	**^{232}Th (STD) (ppm)**	**^{238}U (KED) (ppm)**	**^{238}U (STD) (ppm)**
Method 1	10 mL HF+ 15 mL HNO_3 + 5 mL $HClO_4$	5.23	5.25	1.51	1.54
Method 2	Method 1 + 5 mL HNO_3	5.35	5.44	1.58	1.59
Method 3	Method 1 + 5 mL HF	5.41	5.52	1.75	1.78
Method 4	Method 1 + 5 mL $HCLO_4$	5.42	5.57	1.61	1.66

Table 5: Percent recovery of optimised acid digestion method with increased volumes

Test 3	Acid digestion methods	% Recovery for ^{232}Th (KED)	% Error for ^{232}Th (KED)	% Recovery for ^{232}Th (STD)	% Error for ^{232}Th (KED)	% Recovery for ^{238}U (KED)	% Error for ^{238}U (STD)	% Recovery for ^{238}U (STD)	% Error for ^{238}U (STD)
Method 1	10 mL HF+ 15 mL HNO_3 + 5 mL $HClO_4$	98.58	1.32	99.05	0.94	98.27	1.95	99.80	0.00
Method 2	Method 1 + 5 mL HNO_3	100.97	0.94	102.57	2.64	102.24	2.60	102.91	3.25
Method 3	Method 1 + 5 mL HF	102.17	2.08	104.23	4.15	113.28	13.64	115.21	15.58
Method 4	Method 1 + 5 mL $HCLO_4$	102.23	2.26	105.06	5.09	104.76	4.55	107.74	7.79

5.1.2 Comparison of STD and KED gas mode results

The results from ICP-QMS, using STD mode (consisting of argon gas) and KED mode (consisting of helium gas) as reaction gas produced consistent and comparable results as seen in Table 4 and Table 5. This was monitored using the hot plate acid digested GXR-6. In both modes for method 1 the CRM passed (was within specification), and the results were within the certified values of lower and upper limit. GXR-6 Th lower and upper intervals are 5.08 ppm and 5.52 ppm, U lower and upper intervals are 1.47 ppm and 1.61 ppm.

Figure 5 shows a graphical representation of Table 4 which compares the KED and STD mode results for GXR-6 from hot plate acid digestion. The ^{232}Th results are represented in Figure 5a, which shows the trend of the concentration increasing from method 1 to method4 for both STD mode and KED mode. The STD mode for ^{232}Th in method 3 and method 4 produced results which were higher than the

confidence interval of GXR-6. It can also be observed that the STD mode produced slightly higher concentration than the KED mode in all four methods which are projected in Figure 5a and Figure 5b, however the results presented in Figure 5 may be biased as when more analysis was carried out the internal standard recoveries for STD and KED mode would fluctuates. For ^{238}U which is represented in Figure 5b, the bars show a trend of increase in concentration in the ascending order from method 1, method 2, method 4 followed by method 3 which had the highest recovery.

The results for ^{238}U in method 3 and method 4 produced recoveries which were greater than the highest confidence limit interval (1.61 ppm) of GXR-6 in both STD and KED modes. According to the results presented in Table 4, the STD mode gave slightly higher results for both radioisotopes compared to the KED mode. This could be due to the Kinetic energy discrimination (KED) effect which reduces polyatomic ion interferences originating from the plasma or vacuum interface in collision cell during sample analysis, hence the results are slightly high. The high results on the STD could also be due to any other contaminations in the instrument. In overall, the results shows that there is less than 5% difference between the concentrations of the STD and the KED modes for both ^{238}U and ^{232}Th.

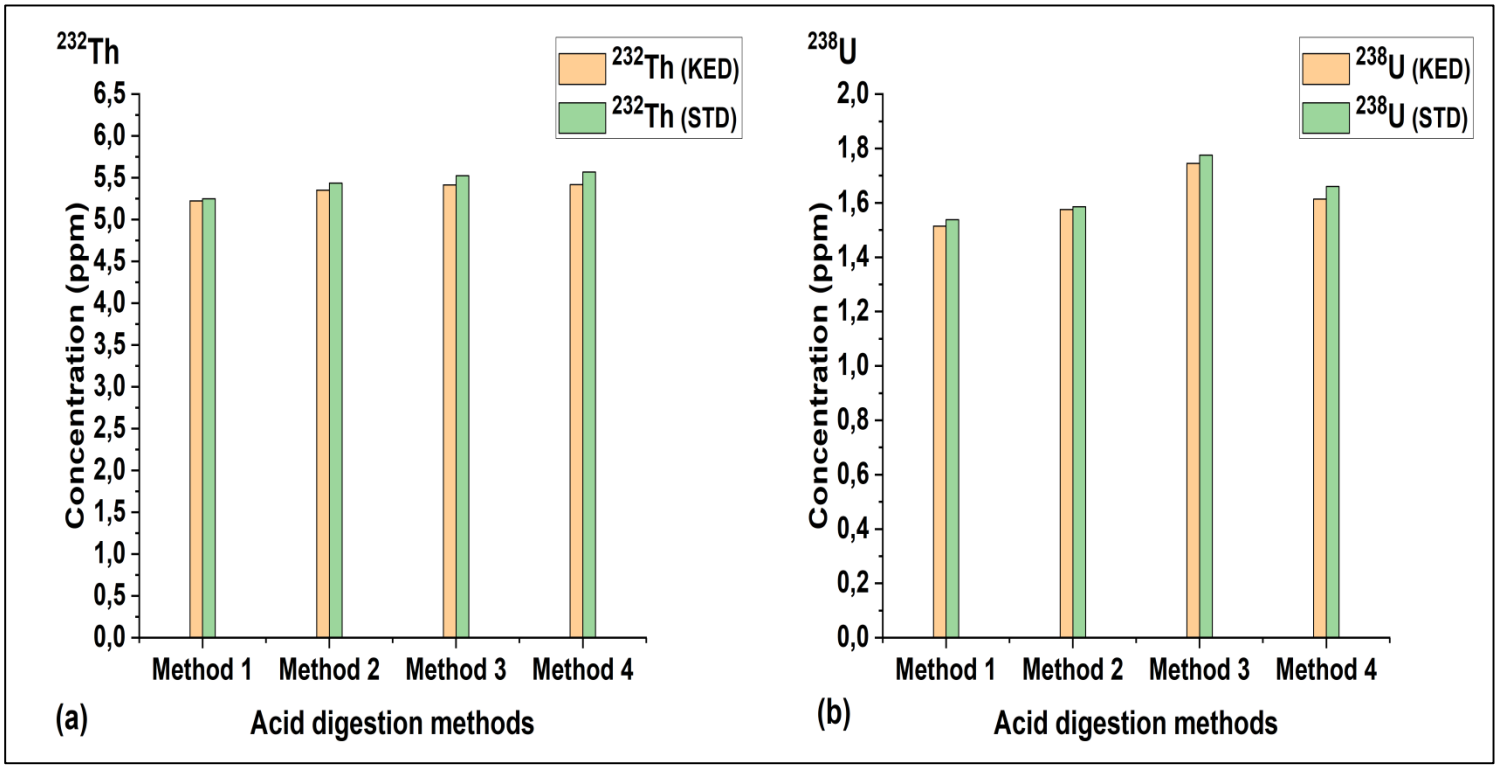


Figure 5: (a) Shows the comparison of different hot plate acid digestion methods of GXR-6 for ^{232}Th STD and KED mode. (b) Shows the comparison of different hot plate acid digestion methods of GXR-6 for ^{238}U STD and KED mode

5.1.3 Calibration curves of U and Th radioisotopes

The calibration was prepared using the prepared stock solution of the multi element standard and the single element standards of U and Th. Two calibration ranges were used, one ranged from 5 to 50 ppb and another from 5 to 100 ppb. The calibration curves of ^{238}U, ^{232}Th,^{232}U and ^{235}U produced good calibration curves whereas the calibration curves of ^{228}Th, ^{229}Th, ^{230}Th, ^{233}U, ^{234}U, and ^{236}U were not satisfactory. The calibration curves are provided in Appendix A.

The calibrations of ^{232}Th and ^{232}U showed good calibration curves for both STD and KED mode with the r-squared values of 0.9999 for the STD mode and 0.9998 for the KED mode. Both calibration curves had low background equivalent concentration (BEC) of 0.1220 ppb for STD mode and 0.1150 ppb for KED mode for ^{232}Th. The limit of detection (LoD) values was 0.0014 ppb for STD mode and 0.0043 ppb for the KED mode. For ^{232}U the BEC and LoD were 0.1220 ppb mode and 0.0025 ppb for the STD mode and 0.1170 ppb and 0.0059 ppb for the KED mode. However, the isotope ^{232}U is less abundant in nature and produced results which were like that of ^{232}Th. The result for ^{232}Th and ^{232}U were similar due to interference caused by their elemental mass, therefore the concentration of ^{232}U was a

combination of ^{232}U and ^{232}Th. This was due to the ICP-MS principle where Ions are sorted and quantified based on their mass-to-charge (m/z) ratio in the mass analyser.

^{238}U calibration passed with accuracy for both STD and KED mode, this was due to its high abundance in both the standards, and it can be seen in Appendix A. The r-squared values in the calibration curves were 1.0000 for the STD mode and 1.0000 for the KED mode. The BEC and LoD were low, 0.4250 ppb and 0.0103 ppb for STD mode and 0.4220 ppb and 0.0085 ppb for the KED mode.

The standards used in this study did not contain or provide information of the specific radioisotopes of U and Th. Hence the most abundant radioisotopes of ^{238}U and ^{232}Th produced better calibration curves. For radioisotopes such as ^{228}Th, ^{229}Th and ^{230}Th the calibrations did not pass for both STD and KED mode. ^{228}Th had poor regression line, with the r-squared value of less than 0.1 for both modes. It also has high BEC concentration of 223.9900 ppb and high LoD of 43.1070 ppb for the STD mode and low BEC and LoD for the KED mode. ^{229}Th had a poor calibration curve with regression lines having a negative slope for STD mode.it has negative r-squared value and a negative BEC concentration. The limit of detection could not be detected due to the negative slope. The KED mode for ^{229}Th also had a negative slope but with 0 ppb BEC and LoD. ^{230}Th also had poor calibration curve with the regression line. This led to it having a negative slope for the STD mode, a negative r-squared value and negative BEC concentration. The limit of detection could not be detected due to the negative slope. The KED mode had 0.6433 r-squared value which was low, with high BEC of 33.4540 ppb and high LoD of 173.8300 ppb. Therefore, these radioisotopes could not be analysed because of their poor calibration curves.

^{233}U and ^{234}U calibrations did not pass on the STD mode, whereas for the same isotopes in KED mode the calibrations passed. ^{233}U showed poor calibration curve for STD mode, with an r-squared value of 0.8047, a high BEC concentration of 27.5600 ppb and a high LoD of 5.9083 ppb. The KED mode had a better r-squared value of 0.9943 and a low BEC concentration compared to the STD mode. However, the LoD was high (1.6369 ppb). The calibrations for this radioisotope were poor as it can also be seen on Appendix A. ^{234}U also showed poor calibration curve for STD mode, with an r-squared value of 0.9452, it also had a high BEC concentration of 29.0340 ppb and a high LoD of 58.5623 ppb. The KED mode had a better r-squared value of 0.9994 but it also had a high BEC concentration of 1.3960 ppb and the LoD of 7.2534. Therefore, the calibration curves for these radioisotopes were poor and no analysis could be performed using these calibrations.

^{235}U calibration passed for both STD and KED mode, the r-squared values were 0.9994 for the STD mode and 0.9999 for the KED mode. Both modes had greater than 1.0000 ppb for BEC and slightly high LoD concentration of 0.8264 ppb for STD mode and 0.3900 ppb for the KED mode. However, the results could not be reported due to the high BEC and since the CRM GXR-6 was not certified for ^{235}U. ^{236}U calibrations also did not pass due to its poor regression line, with an r-squared value of 0.9296, a high BEC concentration 7.8570 ppb and a high LoD of 16.2904 ppb. The KED mode had an r-squared value of 0.9594, a low BEC and a LoD concentrations of 0 ppb. The calibrations for this radioisotope were poor and therefore the results could not be reported due to its poor calibration curve, low abundance, and lack of its presence on the calibration standards.

5.1.4 Recovery of internal standard and samples

Figure 6 shows the percent recovery of the internal standards of indium and rhenium in both KED and STD mode after the analysis of GXR-6. The graph is plotted against the row index number, which is the number that corresponds to the sample analysed in that specific position. The average recovery of indium (^{115}In) was determined to be 105.54% for KED mode and 99.36% for STD mode. The average recovery of rhenium (^{187}Re) was determined to be 111.19% for KED mode and 104.97% for STD mode for CRM GXR-6. The significance difference when using indium and rhenium as internal standards was the masses of their isotopes. This had a slight impact on the CRM's results based on the internal standards chosen to process the results. The choice of internal standard in the ICP-MS should have a close mass to that of the radioisotope of interest. However internal standards with low relative mass to the radioisotopes can still be used since the performance of the internal standards behave differently to different sample matrices.

When using Indium as the internal standard, the recovery of the GXR-6 would become slightly lower but still within the confidence limit intervals. When the results are processed using Rhenium as the internal standard, the results would become slightly higher compared to when they were processed with Indium. The results would still be within the confidence limit interval or slightly higher when either ^{115}In or ^{187}Re was used. Figure 6a represents the internal standard recovery of Indium for both KED and STD mode during GXR-6 analysis. The recovery for indium in STD mode was higher than the recovery in the KED mode. Figure 6b represents the internal standard recovery of Rhenium for both KED and STD mode. The STD mode had higher recoveries compared to the KED mode. ^{187}Re had a close mass to the masses of the radioisotopes of ^{232}Th and ^{238}U compared to ^{115}In. However, there was no significant difference in the results when they were processed using ^{115}In or ^{187}Re as the internal standards.

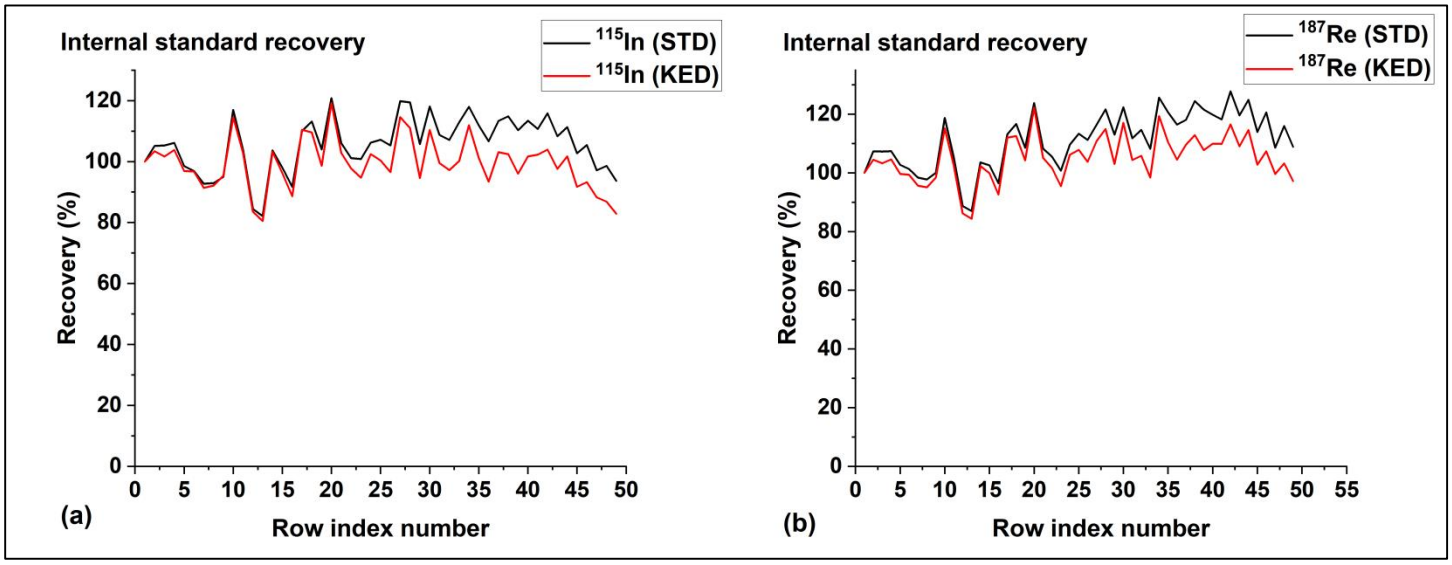


Figure 6: (a) Shows a comparison of the internal standard recovery of Indium (^{115}In) in both KED and STD mode for GXR-6 CRM. (b) Shows a comparison of the internal standard recovery of Rhenium (^{187}Re) in both KED and STD mode for GXR-6 CRM

5.1.5 Optimisation of the column Resins

5.1.5.1 Separation optimisation results

The separation and preconcentration optimisation were done using the hot plate acid digested CRM GXR-6 and the resin used was AmberChrom 1x8 50-100 mesh. Note, all eluates per experiment were collected into 24 vials, making up a total of 24 different fractions. Vial 1 to 12 contained eluates from HCl solvents and vial 13 to 24 contained eluates from Milli-Q water.

5.1.5.2 Effect of the sample's eluate pH

Figure 7 (a-d) shows the graphs of ^{238}U and ^{232}Th concentrations and pH for the separated fractions. There was no pH stability throughout the experiments as it fluctuated depending on the concentration of the ^{238}U and ^{232}Th contained on each fraction. However, graphically a trend was observed on Figure 7. It was observed that at a pH between 0.38 and 1.07, ^{232}Th was obtained and ^{238}U was obtained at a pH between 0.55 and 1.72. The pH for ^{238}U was increasing due to the eluent used which was Milli-Q water. An overlap of the two radioisotopes in the separated fractions at pH between 0.55 and 1.07 was also observed for the 1 M, 2 M, and 3 M HCl eluted fractions. The pH trend showed a slight increase where the radioisotopes of interests were detected in high concentration and a decrease when the concentration of the radioisotopes of interest decreased. This however it did not apply to all the fractions containing high concentrated radioisotopes. A shift could be noticed where in at 4 M HCl separation of

a 20 mL sample load, the fractions had a pH of 0.46 with ^{232}Th concentration of 4.68 ppm and at a pH of 0.64 the ^{232}Th concentration was 2.42 ppm which was lower than concentration at pH of 0.46. This proves that the pH of the separated and concentrated CRM did not have an effect on the results ^{238}U and ^{232}Th.

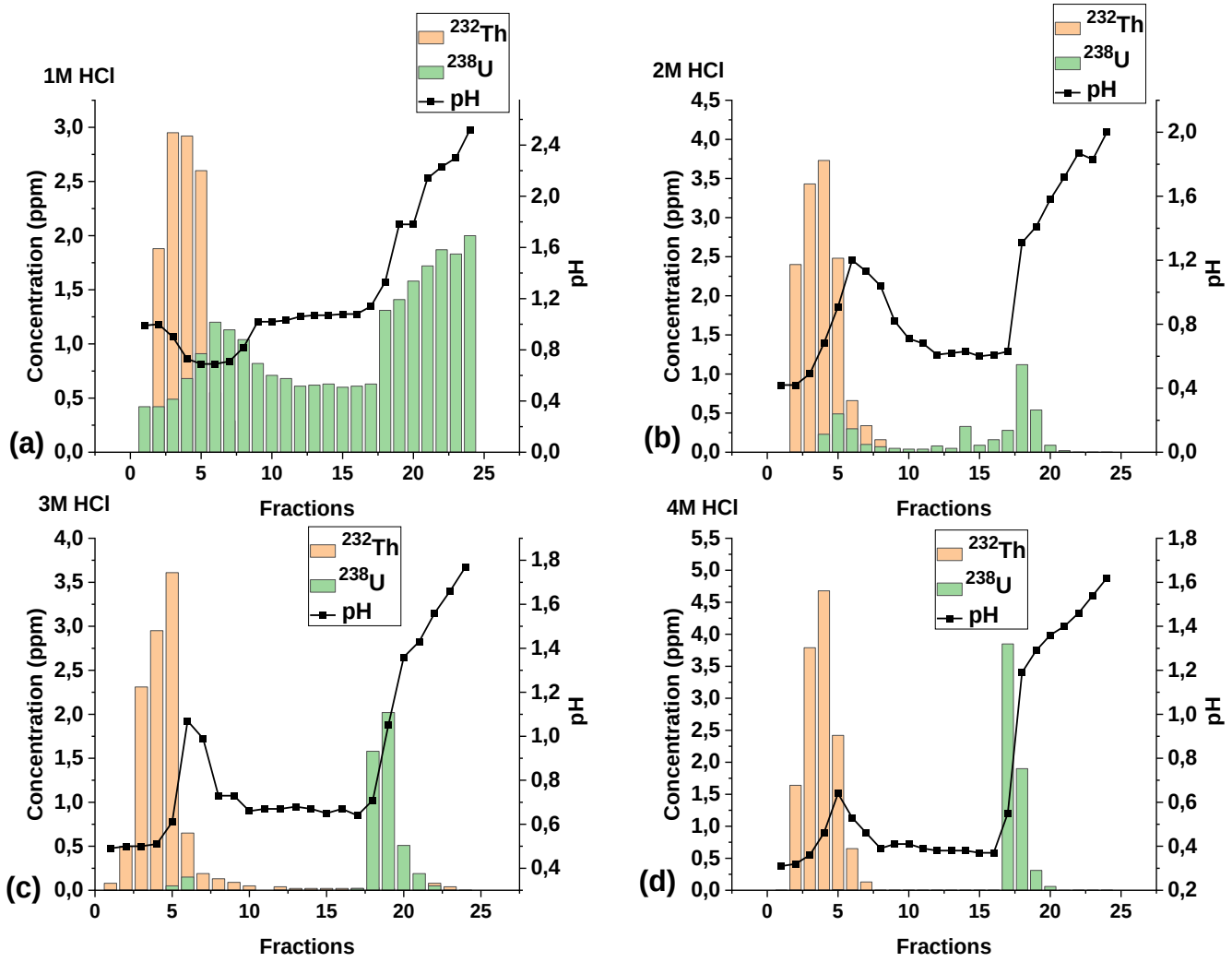


Figure 7: (a) Effect of pH for 1 M HCl separation of ^{232}Th and ^{238}U; (b) Effect of pH for 2 M HCl for separation of ^{232}Th and ^{238}U; (c) Effect of pH for 3 M HCl for separation of ^{232}Th and ^{238}U; (d) Effect of pH for 4 M HCl for separation of ^{232}Th and ^{238}U

5.1.5.3 Effect of the loaded Sample Volume

5.1.5.3.1 At 10 mL sample load

The results of the separation and preconcentration of 10 mL loaded samples are shown in Figure 8a. Poor separation of ^{232}Th from ^{238}U was observed, however, preconcentration of ^{238}U was obtained between vial 18-19 where 3.55 ppm of ^{238}U was recovered. The highest concentration of ^{232}Th

recovered was 2.82 ppm. Which was low, hence preconcentration of ^{232}Th was not achieved. Peaks of ^{232}Th and ^{238}U were also observed from vial 1 to vial 24. This proved that 10 mL sample loaded on a 50 mL reservoir was not enough to be separated or preconcentrated, hence poor separation results were observed. The separation of the 10 mL sample load was not successful as it can be seen on Figure 8a where there were visible peaks of both ^{238}U and ^{232}Th throughout the fractions.

5.1.5.3.2 At 15 mL sample load

At 15 mL sample load the ^{232}Th and ^{238}U peaks observed were few compared to the 10 mL sample load in Figure 8a. Figure 8b shows the traces of ^{238}U concentrations which was observed on the first 12 fractions where 4 M HCl was used as an eluent, whereas there were no traces of ^{232}Th when Milli-Q water was used as the eluent to elute ^{238}U from the column resin. The volume of 15 mL was still not enough to perform a complete separation and preconcentration of ^{232}Th and ^{238}U.

5.1.5.3.3 At 18 mL sample load

Figure 8c shows results of the 18 mL sample load where ^{232}Th was eluted and recovered from vial 1 to 14 with the highest recovery of 3.29 ppm. From the collected ^{232}Th fractions, separation and preconcentration of ^{232}Th was not achieved due to low recovery. Traces of ^{238}U were observed between fractions 4 to 12. Traces of ^{232}Th which co-eluted with ^{238}U at vial 13 and 14 was observed where Milli-Q water was used as the eluent. This also led to poor separation of these radioisotopes, even though ^{238}U was preconcentrated with the highest recovery of 6.15 ppm which was also greater than that of the certified GXR-6 (1.47 ppm)

5.1.5.3.4 At 20 mL sample load

At 20 mL sample load, the separation of ^{232}Th from ^{238}U was achieved as it can be seen in Figure 8d, which shows two sharp peaks of ^{232}Th and ^{238}U. The separation was better than that of sample load of 10 mL, 15 mL, and 18 mL. High concentration recovery of ^{232}Th after separation was observed and the concentration was 4.68 ppm which was collected in vial 4. From vial 13 to vial 24 there were no traces of ^{232}Th observed under the ^{238}U peak, however a 0.01 ppm trace of ^{238}U was observed under the ^{232}Th peak. Higher concentration of ^{232}Th could not be achieved as some concentrations were recovered in the first 7 vials. The highest recovered concentration of ^{238}U was 3.85 ppm. Separation of the two radioisotopes was partially achieved, with ^{238}U being preconcentrated and ^{232}Th under recovering.

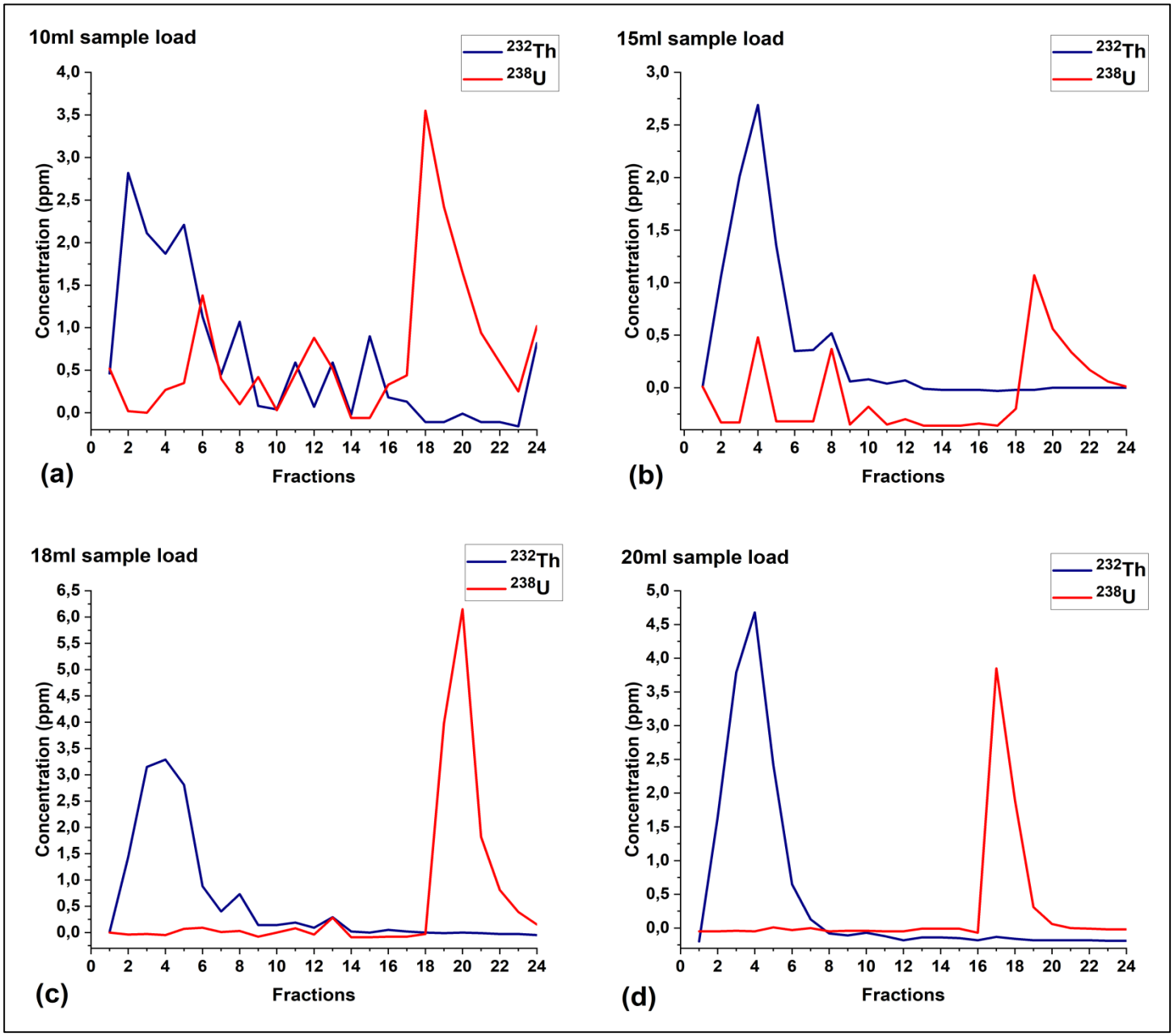


Figure 8: (a) 10 mL sample load of 4 M HCl separation; (b) 15 mL sample load of 4 M HCl separation; (c) 18 mL sample load of 4 M HCl separation; (d) 20 mL sample load of 4 M HCl separation

5.1.5.4 Effect of HCl elution solvent concentration and Milli-Q water

The results for the variation of HCl concentrations and Milli-Q water are represented in Figure 9(a-e). The separation of ^{232}Th from ^{238}U using 1 M HCl was not efficient as it can be seen in Figure 9a. ^{232}Th and ^{238}U co-eluted when 1 M HCl was used as an eluent with the highest recovery of ^{232}Th being 2.95 ppm and ^{238}U being 0.77 ppm. Traces of ^{238}U were observed in the first 10 fractions where only ^{232}Th was expected. This shows that at low HCl concentration ^{238}U does not adsorb to the resin. In this separation, there was no preconcentration of the radioisotopes.

The separation using 2 M HCl eluent was also not efficient as it can be seen in Figure 9b. Traces of ^{238}U were observed under the ^{232}Th peak whereas, no ^{232}Th traces were observed when Milli-Q water was used to elute ^{238}U. However, 2 M HCl produced better separated results compared to 1 M HCl and ^{232}Th and ^{238}U were not preconcentrated.

The separation of ^{232}Th from ^{238}U results using 3 M HCl eluent is shown in Figure 9c. The peaks of ^{232}Th and ^{238}U are well separated, however small traces of ^{238}U were observed under the ^{232}Th peak. Traces of ^{232}Th were also observed from vial 13 to 23 under the ^{238}U peak. The separation using 3 M HCl produced better results than the separations of 1 M and 2 M HCl. Only ^{238}U was preconcentrated with the recovery of 2.02 ppm. The highest recovery amount for ^{232}Th was 3.61 ppm which was low.

^{232}Th and ^{238}U were well separated with 4 M HCl eluent as it can be observed In Figure 9d. 4 M HCl eluent eluted ^{232}Th and Milli-Q water eluted ^{238}U. It was observed that when HCl solvents concentration was increased, ^{232}Th was eluted whereas ^{238}U was adsorbed onto the resin. Hence traces of ^{238}U were as low as 0.01 ppm under the ^{232}Th peak. The highest concentration recovery for ^{232}Th was 4.68 ppm which was still lower than the GXR-6 lowest certified interval (5.08 ppm). ^{232}Th preconcentration was not achieved. From vial 16 to 20 ^{238}U eluted and there were no traces of ^{232}Th observed since it eluted when 4 M HCl was used. The highest recovered concentration for ^{238}U was 3.85 ppm which was greater than GXR-6 highest certified interval (1.61 ppm). ^{238}U was preconcentrated in this separation and the separation of ^{232}Th from ^{238}U was partially achieved due to the 0.01 ppm of ^{238}U the ^{232}Th fraction.

^{232}Th was eluted and separated from ^{238}U using 8 M HCl eluent as it can be observed in Figure 9e. The separation of ^{232}Th from ^{238}U was not successful as there were constant traces of contaminations of both ^{232}Th and ^{238}U from vial 3 to 24. This may have been caused by leaks around the stopcock during the elution process. ^{238}U was preconcentrated whereas ^{232}Th was not. Nevertheless, Figure 9e shows well separated peaks. Even though in this experiment the separation was not successful.

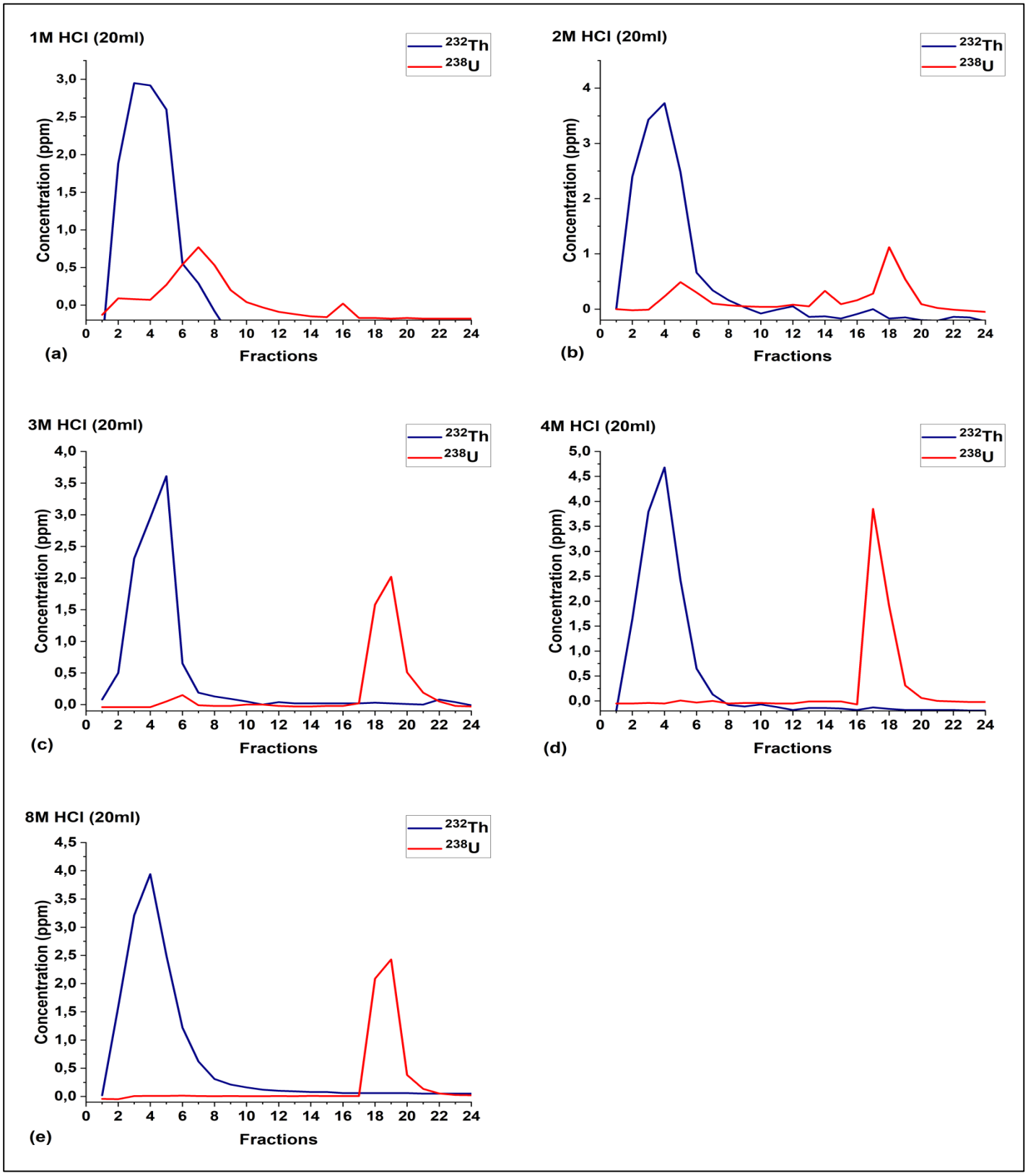


Figure 9: (a) Effect of 1 M HCl for the separation of ^{232}Th from ^{238}U; (b) Effect of 2 M HCl for the separation of ^{232}Th from ^{238}U; (c) Effect of 3 M HCl for the separation of ^{232}Th from ^{238}U; (d) Effect of 4 M HCl for the separation of ^{232}Th from ^{238}U; Effect of 8 M HCl for the separation of ^{232}Th from ^{238}U

5.1.5.5 Effect of sample contact time

5.1.5.5.1 Separation of <1 minute, 10 minutes, and 30 minutes sample contact time with the resin

The results for the effect of time are presented in Figure 10(a-c). The contact time of the samples in the column resin had slightly low effect on the separation and preconcentration recoveries of ^{232}Th and ^{238}U. It can be observed in Figure 10a-c that both ^{232}Th and ^{238}U were separated from each other. All three graphs (a-c) produced ^{232}Th recoveries which were between 3.50 ppm - 4.00 ppm. The recoveries were below the GXR-6 lower limit of confidence interval. This was caused by the collected fractions where ^{232}Th was distributed into different vials. ^{232}Th eluted from clear and yellow bands which made it difficult to collect into one vial. Most of ^{238}U was eluted and collected in vial 18 for all three Figures and the recoveries were all higher than the GXR-6 highest confidence interval limit. Therefore, the contact time of the sample in the resin did not show much effect on the separation, since the radioisotopes are dependent on the eluent used.

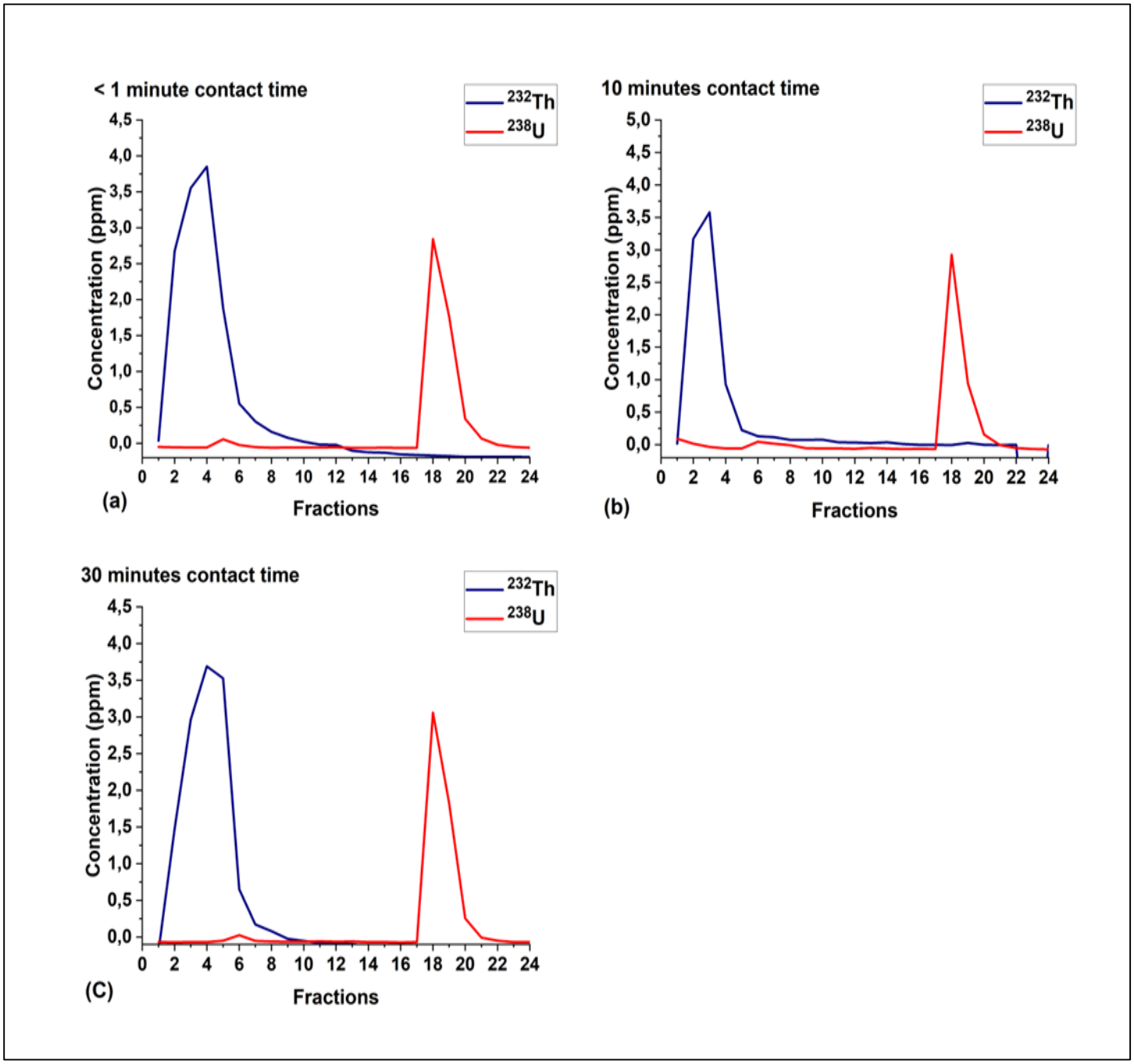


Figure 10: (a) Effect of < 1 minute sample contact time; (b) Effect of 10 minutes sample contact time; (c) Effect of 30 minutes sample contact time

5.2 APPLICATION OF OPTIMISED METHODS

This chapter discusses the results of the application of the optimised methods. The mine tailings samples (sample 1(483) and sample 2(488)) and soil CRMs (GXR-6 and OREAS 45e) were prepared using the hot plate acid digestion method (method 1, in test 3) which incorporated the use of the four acid mixtures (HF+ HNO_3 + $HClO_4$ + H_2O_2). The hot plate acid digested samples were analysed before and after the column resin separation and preconcentration process by ICP-QMS. From the optimised method, a 20 mL sample load, a 10-minute sample contact time, the eluents (4 M HCl solvent, 8 M HCl solvent and Milli-Q water) were chosen as the most suitable parameters to conduct the separation and preconcentration of ^{238}U and ^{232}Th in the column resin. This method was applied to the three AmberChrom resins (AmberChrom 1X8 20-50 mesh, AmberChrom 1X8 50-100 mesh and AmberChrom 1X2 50-100 mesh).

5.2.1 Hot plate acid digestion results

The hot plate acid digestion results for the samples and CRMs are reported in Table 6.1. The method yielded good recoveries for both CRMs (GXR-6 and OREAS 45e) and samples (sample 1(483) and sample 2(488)) which were prepared in triplicates. The percent recoveries, the average for GXR-6 were 98% and 99.31% for ^{238}U and ^{232}Th with the %RSD of 1.10% and 0.49%. For OREAS 45e the recoveries were 102.21% and 101.24% for ^{238}U and ^{232}Th with the %RSD 1.55% and 0.87%.

From the hot plate acid digested samples in Table 6.1, ^{232}Th and ^{238}U were separated using three different AmberChrom resins (1x2 50-100 mesh; 1x8 20-50 mesh and 1x8 50-100 mesh), with the aim of separating and preconcentrating these radioisotopes. As reported in chapter 5.1.5, AmberChrom 1x8 50-100 mesh was optimised in order to identify the best separation parameters. The optimised method was applied to all three resins during separations. From the triplicates prepared, the samples and CRMs were distributed to each resin for separation as presented in Table 6.1. All raw data in this chapter is attached from appendix M to Y.

Table 6.1: Shows the hot plate acid digested data which were used for separation for each resin

	AmberChrom resin 1x8 50-100 mesh		**AmberChrom resin 1x8 20-50 mesh**		**AmberChrom resin 1x2 50-100 mesh**	
Samples	**^{232}Th (ppm)**	**^{238}U (ppm)**	**^{232}Th (ppm)**	**^{238}U (ppm)**	**^{232}Th (ppm)**	**^{238}U (ppm)**
GXR-6	5.25	1.51	5.26	1.51	5.28	1.53
OREAS 45e	12.94	2.49	12.97	2.44	13.27	2.47
Sample 1(483)	12.61	61.85	12.06	63.79	12.12	60.58
Sample 1(488)	1.10	4.17	1.14	4.07	1.07	4.07

5.2.2 Separation and preconcentration using AmberChrom 1x8 50-100 mesh resin using 4 M HCl solvent and Milli-Q water

AmberChrom 1X8 50-100 mesh resin was a pale yellow (white yellow tan), tiny spherical beads. It consists of a quaternary ammonium matrix active group. This resin showed no difficulties in packing as it packed easily. There was no compression or expansion during the resin preconditioning. The resin was more stable during packing compared to AmberChrom 1X8 20-50 mesh and AmberChrom 1X2 50-100 mesh which took longer to pack due to their resin sizes. The acid digested samples and CRMs were separated using AmberChrom 1X8 50-100 mesh resin and the results are presented in Figure 11(a-d). From the separation, the collected fractions from vial 1 to 12 were expected to contain only ^{232}Th as 4 M HCl was used as an eluent. Furthermore, fractions from vial 13 to 24, only ^{238}U was expected to have been collected since Milli-Q water was used as an eluent.

^{232}Th and ^{238}U were separated by AmberChrom 1x8 50-100 mesh resin. ^{232}Th recovery after separation was possible, however it could not be preconcentrated from the separation in all the samples and CRMs. The collection of ^{232}Th fractions during separation proved to be difficult as it eluted readily. Part

of the ^{232}Th fraction eluted on the clear colour band and some eluted on the yellow band. There was no clear indication as to where the highest concentrated ^{232}Th could be collected. The collected fractions had lower recoveries compared to the non-separated ^{232}Th from the samples and CRM's. The lower recoveries were caused by the ^{232}Th eluate being distributed to different vials or fractions. The low recovery of ^{232}Th was observed in all the three AmberChrom resins. The results of the separation of GXR-6, OREAS 45e, sample 1(483) and sample 2(488) by AmberChrom 1x8 50-100 mesh resin are presented in Figure 11 (a-d).

In Figure 11a the separation of ^{232}Th from ^{238}U from GXR-6 CRM was observed, however there was a small trace of ^{238}U (0.06 ppm) under the ^{232}Th peak, this ^{238}U eluted in the ^{232}Th yellow band during separation. In this separation, ^{232}Th recovery after separation was possible. However, ^{232}Th was distributed into more than four fractions. The highest ^{232}Th recovery was 3.78 ppm, which was collected in vial 4 followed by 3.06 ppm and 2.29 ppm which was collected in vial 3 and 5. ^{232}Th highest recovery was 71.98% and it was under recovered.^{238}U recovery after separation was greater than 100%, the concentration before the separation was 1.52 ppm and the concentration obtained after the separation and preconcentration was 2.55 ppm.

OREAS 45e was separated and the results are presented in Figure 11b which shows better separation of ^{232}Th from ^{238}U. From this separation ^{232}Th had lower recovery after separation, which was also caused by it being distributed into more than 2 vials. The highest recovered concentration for ^{232}Th was9.69 ppm collected in vial 3, followed by 9.16 ppm and 7.18 ppm collected in vial 4 and 2. ^{232}Th highest recovery was 74.91%. ^{238}U had better recovery with less concentration distributed into different vials. The highest ^{238}U recovery was 3.32 ppm which was also greater than 100%. ^{238}U was preconcentrated in this separation.

Sample 1(483) in Figure 11c which had high concentrations of both ^{232}Th and ^{238}U shows three peaks, one for ^{232}Th and two for ^{238}U. The separation was not successful since there was a high recovery of ^{238}U where only ^{232}Th was expected. Sample 1 (483) contained ^{232}Th concentration of 12.61 ppm and ^{238}U concentration of 61.85 ppm. The highest recovery for ^{232}Th was 10.10 ppm (80.05%) which was less than the initial concentration. The highest recovery for ^{238}U was 54.23 pm which co-eluted with ^{232}Th. ^{238}U eluted where 4 M HCl was used as an eluent. For the second ^{238}U peak, only up to 43.50 ppm of ^{238}U could be recovered using Milli-Q water. The separation of the radioisotopes in this sample was poor. ^{238}U did not adsorb completely to the resin at 4 M HCl medium, this did not agree with the

properties of radioisotopes at high HCl medium reported by Monroy Guzmán, 2016. The separation and preconcentration of ^{232}Th and ^{238}U in this sample were not achieved.

Figure 11d shows the results of separated sample 2(488). The initial concentrations of ^{232}Th and ^{238}U were 1.10 and 4.17 ppm. The sample behaved similarly to sample 1(483) after separation. Both ^{232}Th and ^{238}U eluted under 4 M HCl medium, ^{238}U eluted again when Milli-Q water was used as an eluent. The separation was visible but not successful since ^{238}U co- eluted with ^{232}Th. In this separation their highest recovery for ^{232}Th was 1.04 ppm (94.22%). High ^{238}U recovery obtained was 4.10 ppm (98.36%) which was recovered together with ^{232}Th. Sample 2(488) was not separated nor preconcentrated by this resin.

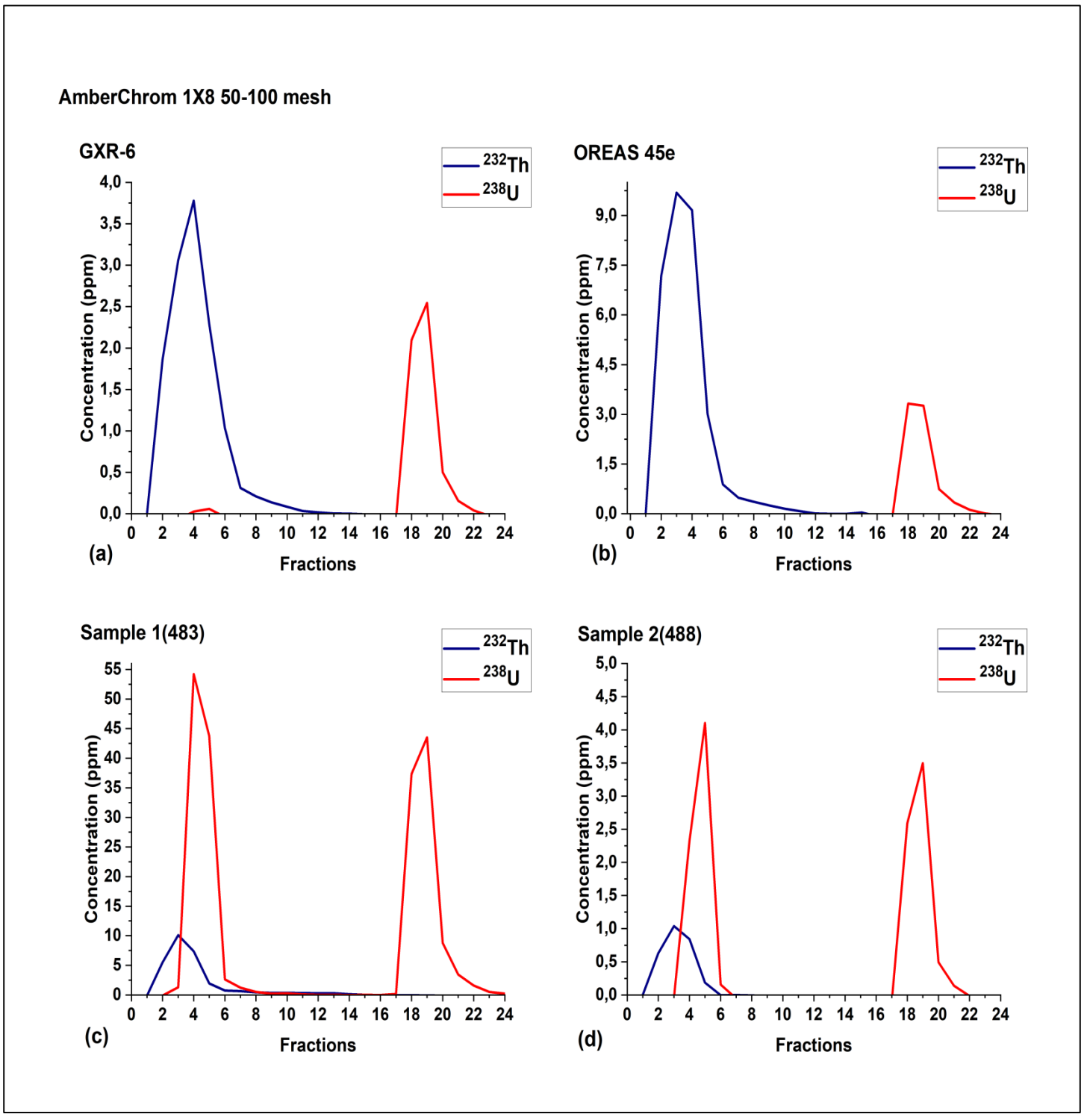


Figure 11: (a) Separation of ^{232}Th from ^{238}U from acid digested GXR-6 by AmberChrom 1x8 50-100 mesh resin; (b) Separation of ^{232}Th from ^{238}U from acid digested OREAS 45e by AmberChrom 1x8 50-100 mesh resin; (c) Separation of ^{232}Th from ^{238}U from acid digested Sample 1(483) by AmberChrom 1x8 50-100 mesh resin; (d) Separation of ^{232}Th from ^{238}U from acid digested sample 2(488) by AmberChrom 1x8 50-100 mesh resin)

5.2.3 Separation and preconcentration using AmberChrom 1x8 20-50 mesh resin using 4 M HCl solvent and Milli-Q water

AmberChrom 1X8 20-50 mesh was a yellow-coloured resin, with bead which are bigger in size when compared to those of 50-100 mesh beads. It consists of a quaternary ammonium matrix active group. Packing of this resin was difficult and time consuming as the resin would destabilise during column preconditioning and sample loading. This made the column resin less stable compared to the other two resins. The size of this resin also influenced the separation or preconcentration of the samples, as the solution introduced during preconditioning could run through the column compared to the other two resins. This resin was used to separate ^{232}Th from ^{238}U from the acid digested CRMs and samples. The results are presented in Figure 12(a-d)

In Figure 12a the separation of ^{232}Th from ^{238}U from the GXR-6 CRM was observed, however there's a trace amount of ^{238}U (0.14 ppm) under the ^{232}Th peak. This trace of ^{238}U eluted in the ^{232}Th yellow band during separation. In this separation, ^{232}Th highest recovered concentration after separation was 3.68 ppm. ^{232}Th was also distributed into more than four fractions, with the highest recovery of 69.95%. ^{238}U recovery after separation was greater than 100%, with the highest concentration of 2.53 ppm. ^{238}U was preconcentrated in this whereas ^{232}Th was not preconcentrated.

Figure 12b shows the recoveries of ^{238}U and ^{232}Th from the separated OREAS 45e. ^{232}Th could not be separated completely from ^{238}U when using 4 M HCl as there is a ^{238}U peak underneath the ^{232}Th peak containing up to 0.62 ppm of ^{238}U. The highest recovery of ^{232}Th in this separation was 9.34 ppm.
The 71.98% recovery of ^{232}Th was still low due to it being distributed into more than 2 vials. ^{238}U had the highest recovery of 2.24 ppm, which is 92.14% of the initial concentration. 0.80 and 0.40 ppm concentrations were distributed into vials 18 and 20 respectively. Both ^{238}U and ^{232}Th were not preconcentrated nor separated from each other.

Sample 1(483) in Figure 12c shows that there was poor separation of ^{232}Th from ^{238}U when 4 M HCl was used as and eluent for both radioisotopes. ^{232}Th and ^{238}U co-eluted in the same vials. However, when Milli-Q water was used as an eluent the remaining ^{238}U was eluted. About 77.71% of ^{232}Th co-eluted with 46.67% of ^{238}U in this separation. When ^{238}U was eluted with Milli-Q water the highest recovery was 52.92% followed by 48.53% in another fraction. In this separation it was difficult to also separate or collect the highest concentrated ^{238}U as the yellow band was dark in colour and very concentrated in both mediums (4 M HCl and Milli-Q water). About 5 mL of the yellow band was collected to avoid the collection of dilute eluates. However, this also led to the ^{238}U concentration being distributed

into different fractions. Separation and preconcentration of ^{238}U and ^{232}Th was not achieved in this sample.

Sample 2(488) results after separation are presented in Figure 12d. The separation trends are like that of sample 1(483). ^{232}Th and ^{238}U of this sample could not be separated using 4 M HCl as both ^{232}Th and ^{238}U peaks co-eluted in the same vials. However, when Milli-Q water was used as an eluent there were no traces of ^{232}Th from the ^{238}U fractions. The highest recoveries in the collected fractions for ^{232}Th and ^{238}U in HCl medium were 42.37% and 27.78%. The highest recovered ^{238}U in Milli-Q water medium was 77.59%, other concentrations were also distributed into different vials. There was poor separation and preconcentration for this sample.

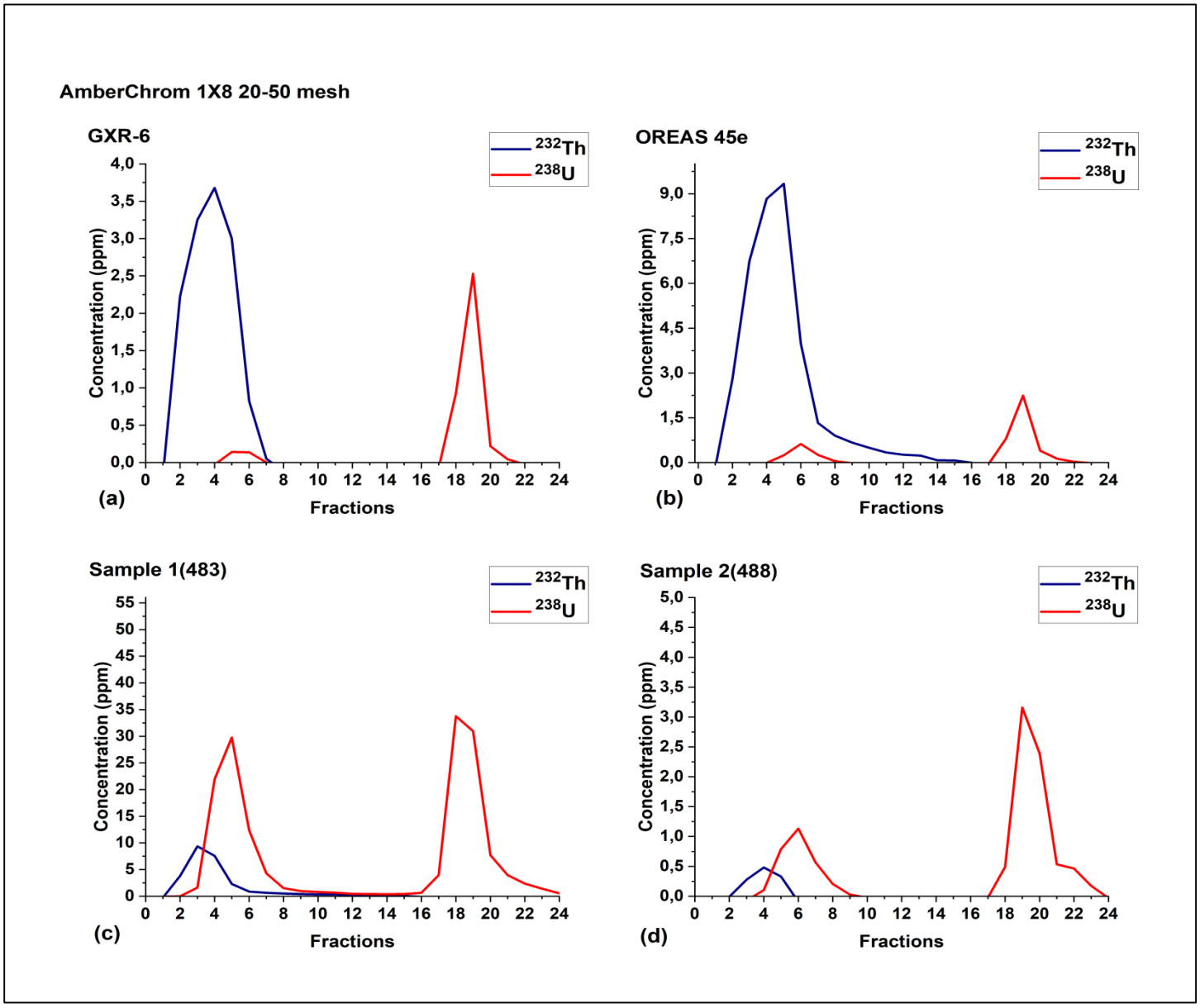


Figure 12: (a) Separation of ^{232}Th from ^{238}U from acid digested GXR-6 by AmberChrom 1x8 20-50 mesh resin; (b) Separation of ^{232}Th from ^{238}U from acid digested OREAS 45e by AmberChrom 1x8 20-50 mesh resin; (c) Separation of ^{232}Th from ^{238}U from acid digested Sample 1(483) by AmberChrom 1x8 20-50 mesh resin; (d) Separation of ^{232}Th from ^{238}U from acid digested sample 2(488) by AmberChrom 1x8 20-50 mesh resin)

5.2.4 Separation and preconcentration using AmberChrom 1x2 50-100 mesh resin using 4 M HCl solvent and Milli-Q water

AmberChrom 1X2 50-100 mesh is a colourless, tiny spherical resin which consists of benzyltrimethylammonium functional group as the matrix active group. The resin was easy to pack, but it reacted with the eluents during the preconditioning step. When 4 M HCl was added to the column the resins expanded and when Milli-Q water was added, the resins compressed. This also had an effect when the samples were loaded and eluted using the two different mediums. Samples and CRMs were separated using this resin and the results are presented in Figure 13(a-d).

The separation results of ^{232}Th from ^{238}U for the acid digested GXR-6 by AmberChrom 1x2 50-100 mesh resin are observed in Figure 13a. ^{238}U was not completely separated from ^{232}Th, as trace amounts of ^{238}U (0.18 ppm) were observed in vial 6. The traces of ^{238}U were not expected between vials 1 and 12 since high HCl medium was used as an eluent. The highest recoveries after the separations were 2.98 ppm (56.39%) for ^{232}Th. In this resin, ^{238}U had greater than 100% recovery of 3.04 ppm and it was preconcentrated.

Figure 13b shows the results of the separated OREAS 45e using 4 M HCl and Milli-Q water as eluents. ^{232}Th and ^{238}U were not completely separated from each other as there were traces of ^{238}U (0.52 ppm) under the ^{232}Th peak. The highest recoveries from this separation were 7.98 ppm (60.71%) for ^{232}Th and 2.79 ppm for^{238}U. ^{238}U was preconcentrated in this resin with greater than 100% recovery.

The results for sample 1(483) are shown in Figure 13c where it can be observed that the separation for the two radioisotopes was poor. However, the highest recovery of ^{238}U was 50.61 ppm (83.54%). which was recovered during the elution with Milli-Q water. ^{232}Th was under recovered and it was contaminated with about 50.89% of ^{238}U. The highest recovered ^{232}Th was 7.14 ppm (58.95%). A complete separation and preconcentration in this sample were not achieved.

Sample 2(488) was not successfully separated and preconcentrated. The results are shown in Figure 13d. The graph shows a similar trend to that of sample 1(483), where there is contamination of about 63.91% (2.60 ppm) of ^{238}U under the ^{232}Th peak. ^{238}U also eluted without any ^{232}Th contamination and its highest recovery was 4.66 ppm which was greater than 100%.). The highest recovered ^{232}Th in this separation was 0.30 (28.45%) which shows that there was poor separation and poor preconcentration of ^{232}Th.

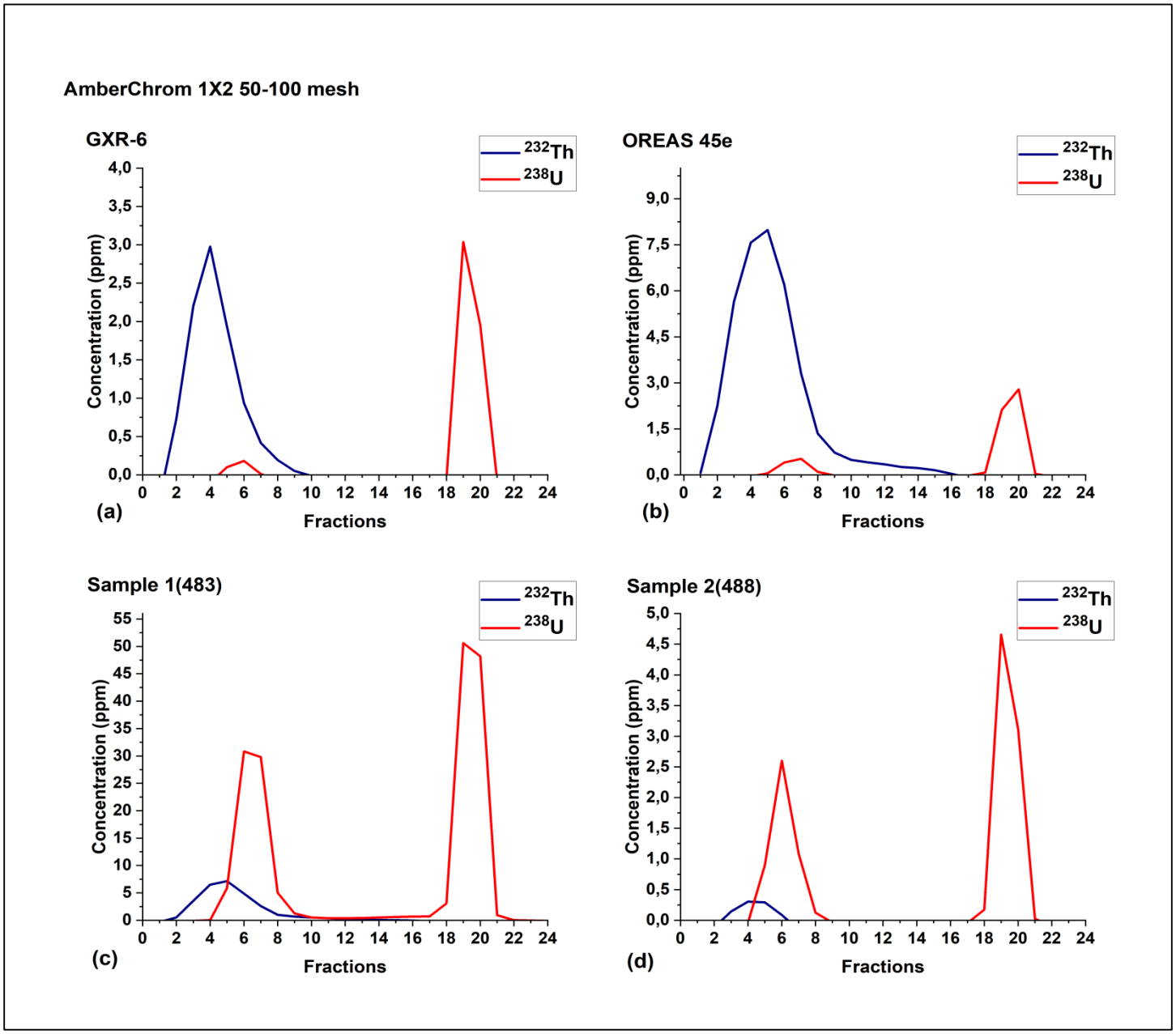


Figure 13: (a) Separation of ^{232}Th from ^{238}U from acid digested GXR-6 by AmberChrom 1x2 50-100 mesh resin; (b) Separation of ^{232}Th from ^{238}U from acid digested OREAS 45e by AmberChrom 1x2 50-100 mesh resin; (c) Separation of ^{232}Th from ^{238}U from acid digested Sample 1(483) by AmberChrom 1x2 50-100 mesh resin; (d) Separation of ^{232}Th from ^{238}U from acid digested sample 2(488) by AmberChrom 1x2 50-100 mesh resin)

5.2.5 Comparison of the resin's separation for each sample and CRMs

The separation and preconcentration efficiency of the three AmberChrom resins on the samples and CRMs were compared. The data comparing the ^{232}Th and ^{238}U highest recoveries after the resin's separation and preconcentration is presented in Table 6.2 and Figure 14. Table 6.2 shows results of the highest recoveries of both ^{232}Th and ^{238}U after separation. ^{232}Th recovery was less than 100% in all the three resins. However, AmberChrom 1x8 50-100 mesh resin produced better recoveries for ^{232}Th followed by AmberChrom 1x8 20-50 mesh resin and by AmberChrom 1x2 50-100 mesh which produced low recoveries.

AmberChrom 1x2 50-100 mesh resin produced greater than 100% ^{238}U recoveries for GXR-6, OREAS 45e and Sample 2(248) which had low concentrations of ^{238}U. This was followed by AmberChrom 1x8 50-100 mesh resin which also produced greater than 100% recoveries for GXR-6 and OREAS 45e. AmberChrom 1x8 50-100 mesh resin had greater than 100% recovery for GXR-6 only. In overall, AmberChrom 1x8 50-100 mesh resin proved to be a better resin for separating and preconcentrating radioisotopes of ^{232}Th and ^{238}U. this resin also yielded better ^{232}Th recoveries compared to AmberChrom (1x8 20-50 mesh and 1x2 50-100 mesh) resins Preconcentration of ^{238}U was possible for the low concentrated samples. Complete ^{232}Th separation and preconcentration were not achieved in all the three resins.

Table 6.2: Shows the highest percent recoveries of ^{232}Th and ^{238}U after separation of each samples and CRMs using the three AmberChrom resins

	AmberChrom resin 1x8 50-100 mesh		**AmberChrom resin 1x8 20-50 mesh**		**AmberChrom resin 1x2 50-100 mesh**	
Samples	**^{232}Th (%)**	**^{238}U (%)**	**^{232}Th (%)**	**^{238}U (%)**	**^{232}Th (%)**	**^{238}U (%)**
GXR-6	71.98	167.88	69.95	168.19	56.39	198.77
OREAS 45e	74.91	111.22	71.98	92.14	60.71	115.46
Sample 1(483)	80.05	87.68	77.71	52.92	58.95	83.54
Sample 2(488)	94.22	98.36	42.37	77.59	28.45	114.39

Figure 14(a-d) shows the comparisons of each sample separated and preconcentrated in each resin. The trend in which ^{232}Th and ^{238}U eluted can be observed in Figure 14 (a-d) in all three resins. ^{232}Th eluted between vials 2 and 6, where it was highly recovered. ^{238}U eluted between vials 17 to 20 in all three resins. However, as it can be observed in Figure 14 there were traces of ^{238}U under the ^{232}Th peaks. These traces in Figure 14a and Figure 14b co-eluted in vial 4 to 8. There were also high recoveries of ^{238}U which eluted from vial 3 to vial 7 in Figure 14c and Figure 14d. This contamination or poor separation was caused by the yellow band which was observed during ^{232}Th elution in all three resins.

GXR-6, OREAS 45e, sample 1(483) and sample 2(488) on the column resins had two yellow bands during elution. The first yellow band was collected in HCl medium, and the second yellow band was eluted with Milli-Q water. The yellow bands were light in colour for GXR-6, OREAS 45e, sample 2(488) which had low ^{238}U concentrations. Dark yellow bands were observed for sample 1(483) which had high ^{238}U concentration. The ^{238}U concentration levels present in the CRMs and the samples proved that 4 M HCl eluent was not efficient to obtain a complete separation of ^{238}U from ^{232}Th in the column resins. Due to the observed contamination of ^{238}U in the ^{232}Th fractions, higher concentrated HCl eluent (8 M HCl) was also used to carry out separation and preconcentration in the AmberChrom 1x8 50-100 mesh resin.

Studies by Alhassanieh *et al*., (1999) and Crespo *et al.,* (2001) reported that Th did not adsorb in the anion Dowex 1X8 resins at high HCl mediums. In this study Th was recovered from 1 M to 8 M HCl eluents. 100% Th recovery was not achieved in any of the HCl mediums as Th readily eluted from the resin and it distributed into different fractions after collection. This proved that Th did not adsorb to the anion AmberChrom resin in HCl medium from 1 M to 8 M HCl concentrations. In contrast to Th, U adsorbed to the resin at high HCl mediums (4 M to 8 M), and it was later eluted with Milli-Q water. However, U at trace levels of 0.01 ppm of was observed in this study at high HCl medium (4 M and 8 M HCl).

Monroy Guzmán, (2016) study discussed the separation of radioisotopes in 4 M to 8 M HCl eluents. Th was recovered using 4 M HCl eluent and 99.2% of Th was obtained after separation using Dowex 1X8 20-50 mesh. U was obtained using H_2O as eluent and the recovery was > 99%. Whereas in this study in the same anion resin AmberChrom (Dowex) 1X8 20-50 mesh about 42.37%, 69.95%, 71.98% and 77.71% of Th for Sample 2(488), GXR-6, OREAS 45e and Sample 1(243) were obtained after separation. These recoveries were obtained from the fraction containing the highest recoveries of Th.

U was eluted using H_2O and the recoveries were greater than 99%, however in this study the recoveries of U differed per sample. U recoveries for GXR-6 was > 100%, whereas for OREAS 45e, Sample 1(243) and Sample 2(248) were 92.14%, 52.92% and 77.59% respectively. This was also affected by the U concentration which eluted at 4 M HCl eluent.

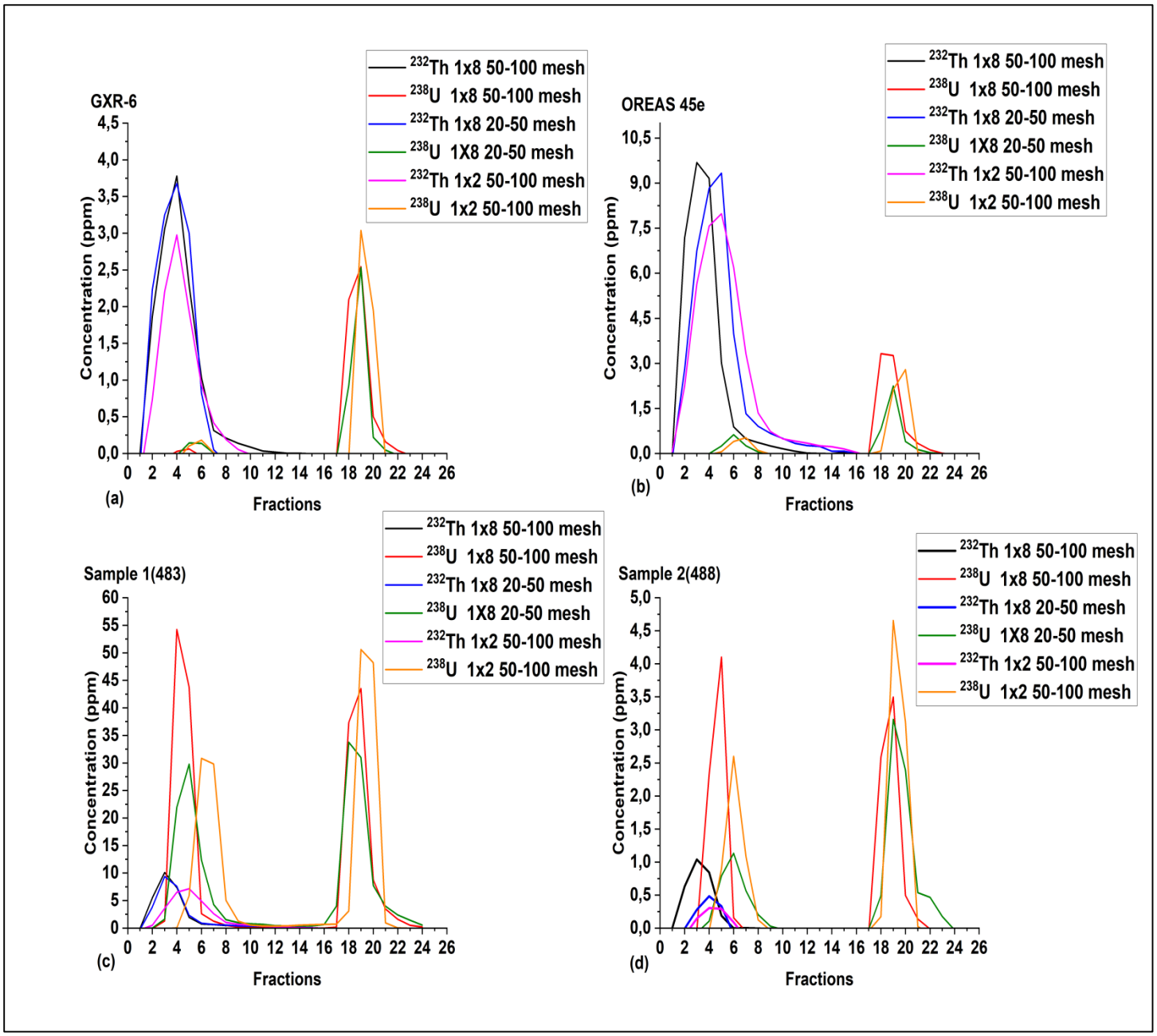


Figure 14: (a) Comparison of separation of GXR-6 by AmberChrom 1x8 50-100 mesh resin, AmberChrom 1x8 20-50 mesh resin and AmberChrom 1x2 50-100 mesh resin; (b) Comparison of separation of OREAS 45e by AmberChrom 1x8 50-100 mesh resin, AmberChrom 1x8 20-50 mesh resin and AmberChrom 1x2 50-100 mesh resin ; (c) Comparison of separation of Sample 1(483) by AmberChrom 1x8 50-100 mesh resin, AmberChrom 1x8 20-50 mesh resin and AmberChrom 1x2 50-

100 mesh resin ; (d) Comparison of separation of sample 2(488) by AmberChrom 1x8 50-100 mesh resin, AmberChrom 1x8 20-50 mesh resin and AmberChrom 1x2 50-100 mesh resin

5.2.6 Separation and preconcentration of ^{238}U and ^{232}Th with 8 M HCl eluent and Milli-Q water in the AmberChrom 1x8 50-100 mesh resin

The use of the 8 M HCl solvent in the column resin was to increase the separation and preconcentration efficiency of ^{238}U and ^{232}Th in sample 1(483), sample 2(488), GXR-6 and OREAS 45e. Figure 15(a-d) shows graphs of the results obtained after separation and preconcentration of the samples and CRMs by 8 M HCl and Milli-Q water in the AmberChrom 1x8 50-100 mesh resin-. The ^{238}U and ^{232}Th highest recoveries of 4 M HCl,8 M HCl eluents and Milli-Q water are shown in Table 7.

GXR-6 separation and preconcentration results are shown in Figure 15a where ^{238}U trace was still observed on the ^{232}Th fractions. Preconcentration of ^{238}U was achieved with greater than 100% (2.40 ppm) recovery. ^{232}Th recovery was 75.12% (4.00 ppm) which was an increase compared to the recovered ^{232}Th when 4 M HCl was used as an eluent. However, ^{232}Th preconcentration was not achieved.

In Figure 15b, OREAS 45e's ^{238}U and ^{232}Th highest recoveries were 3.37 ppm and 10.89 ppm. The recoveries increased when compared to that of 4 M HCl eluent used. Preconcentration of ^{238}U was achieved, however ^{232}Th was not preconcentrated. Complete separation in this CRM was not achieved due to a 0.79 ppm ^{238}U which was found in the ^{232}Th fractions.

An improved separation of ^{238}U and ^{232}Th was observed for Sample 1(483) in Figure 15c. ^{232}Th highest recovery was 7.90 ppm (62.66%), which was lower than the recovery from the 4 M HCl eluent. ^{238}U highest recovery was 90.97 ppm which was greater than 100%. ^{238}U was preconcentrated whereas ^{232}Th was not. The complete separation in this sample was not achieved as there was up to 1.32 ppm traces of ^{238}U in the ^{232}Th fractions. The separation and preconcentration was better than that of 4 M HCl solvent. However, ^{232}Th was best recovered with 4 M HCl solvent.

In Figure 15d, poor separation was observed with up to 1.42 ppm of ^{238}U found in the ^{232}Th fractions. The highest recoveries obtained for ^{238}U and ^{232}Th were 5.13 ppm (>100%) and 0.75 ppm (68.33%) respectively. ^{238}U was preconcentrated whereas ^{232}Th was not preconcentrated. ^{238}U concentration of up to 1.42 ppm was obtained in ^{232}Th fractions. Better separation of ^{238}U and ^{232}Th was observed in 8 M HCl eluent compared to 4 M HCl eluent. However, in this sample ^{232}Th was best recovered with 4 M HCl eluent.

Table 7: Shows the comparison of 4 M HCl and 8 M HCl eluent's highest percent recoveries of ^{232}Th and ^{238}U after separation of samples and CRMs using the AmberChrom 1x8 50-100 mesh resin

	AmberChrom resin 1x8 50-100 mesh (4 M HCl eluent)				**AmberChrom resin 1x8 50-100 mesh (8 M HCl eluent)**			
Samples	**^{232}Th (%) Yield**	**^{232}Th (%) Error**	**^{238}U (%) Yield**	**^{238}U (%) Error**	**^{232}Th (%) Yield**	**^{232}Th (%) Error**	**^{238}U (%) Yield**	**^{238}U (%) Error**
GXR-6	71.98	28.02	167.88	67.88	75.12	24.88	158.45	58.45
OREAS 45e	74.91	25.09	111.22	11.22	82.09	17.91	136.32	36.32
Sample 1(483)	80.05	19.95	87.68	12.32	62.66	37.34	151.93	51.93
Sample 2(488)	94.22	5.78	98.36	1.64	68.33	31.67	122.89	22.89

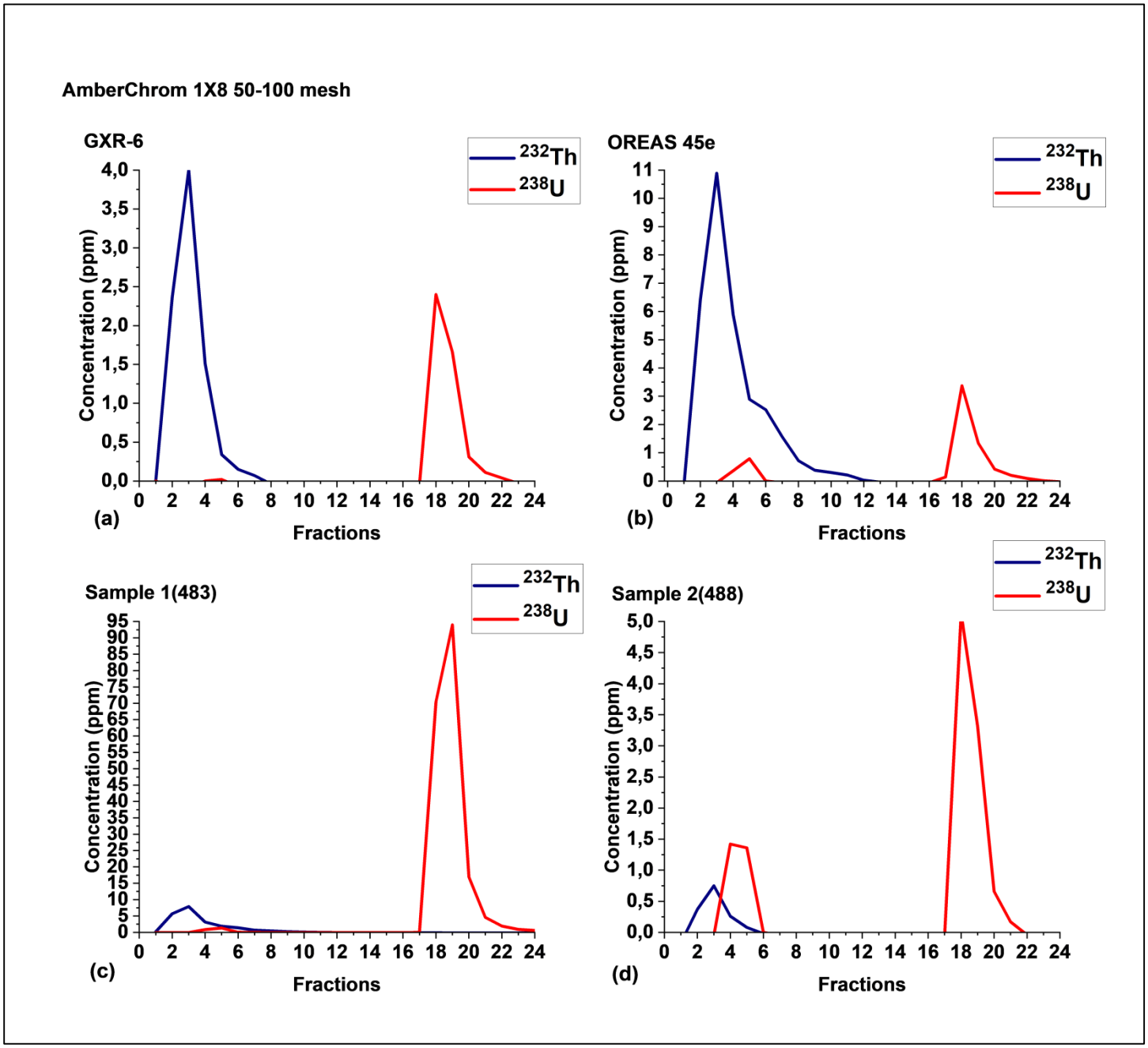


Figure 15: (a) Separation of ^{232}Th from ^{238}U of acid digested GXR-6 by AmberChrom 1x8 50-100 mesh resin using 8 M HCl solvent; (b) Separation of ^{232}Th from ^{238}U of acid digested OREAS 45e by AmberChrom 1x8 50-100 mesh resin using 8 M HCl solvent; (c) Separation of ^{232}Th from ^{238}U of acid digested Sample 1(483) by AmberChrom 1x8 50-100 mesh resin using 8 M HCl solvent; (d) Separation of ^{232}Th from ^{238}U of acid digested sample 2(488) by AmberChrom 1x8 50-100 mesh resin using 8 M HCl solvent.

CHAPTER 6: CONCLUSION

The determination of ^{238}U and ^{232}Th radioisotopes by ICP-QMS was achieved through the extraction of ^{238}U and ^{232}Th from the soil CRMs and mine tailings samples. The four-acid combination HNO_3, HF, $HClO_4$ and H_2O_2 for hot plate acid digestion method proved to be the most efficient sample preparation method which produced greater than 98% recoveries for both ^{232}Th and ^{238}U from GXR-6 and OREAS 45e soil CRMs. The microwave acid digestion method however produced greater than 100% recovery for ^{238}U only and less than 40% recovery for ^{232}Th in these CRMs.

Three anionic based AmberChrom resins (1x8 50-100 mesh resin,1x8 20-50 mesh and 1x2 50-100 mesh) were used in order to enhance the radioisotope's recoveries with the aim of separating and preconcentrating ^{238}U and ^{232}Th from the acid digested CRMs (GXR-6 and OREAS 45e) and mine tailings samples (Sample 1(483), Sample 2(488)). Milli-Q water and various HCl solvents were evaluated for the effective separation and preconcentration of the samples. 4 M HCl solvent was selected as ^{232}Th eluent and Milli-Q water was used to elute ^{238}U. Partial separation was achieved in all three resins, whereas preconcentration of ^{238}U in GXR-6 and OREAS 45e was achieved from AmberChrom 1x8 50-100 mesh and AmberChrom 1x2 50-100 mesh with greater than 100% recoveries. AmberChrom 1x8 50-100 mesh resin proved to produce better recoveries of ^{238}U and ^{232}Th.

A higher HCl eluent, 8 M HCl was used in order to improve the separation and preconcentration of CRMs and Samples in the AmberChrom 1x8 50-100 mesh resin. The 8 M HCl eluent improved the separation method by decreasing the ^{238}U concentrations found in the ^{232}Th fractions. An increase in ^{232}Th recovery was observed for GXR-6 and OREAS 45e, where as a decrease in ^{232}Th recovery was observed for Sample 1(483) and Sample 2(488). ^{238}U recoveries increased for both samples and CRMs and it was greater than 100%. Preconcentration was achieved for ^{238}U, whereas for ^{232}Th it was not. In conclusion partial separation and preconcentration of ^{238}U and ^{232}Th from the acid digested GXR-6, OREAS 45e, Sample 1(483) and Sample 2(488). was achieved using 4 M HCl and 8 M HCl eluent's.

Recommendations

The recommendation is based on the extraction and separation methods, which was not achieved. Future work will be required to improve the microwave acid digestion for the extraction of Th and other radioisotopes. Separation methods can also be developed or extended to ensure that more radioisotopes besides U and Th can be separated and preconcentrated.

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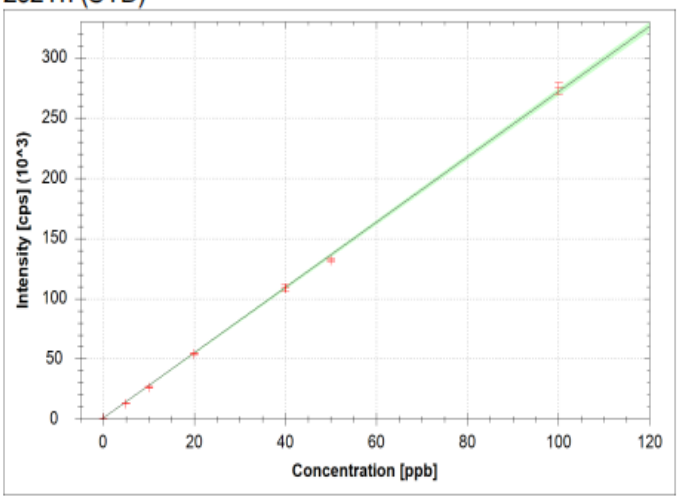
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APPENDICES

Appendix A:

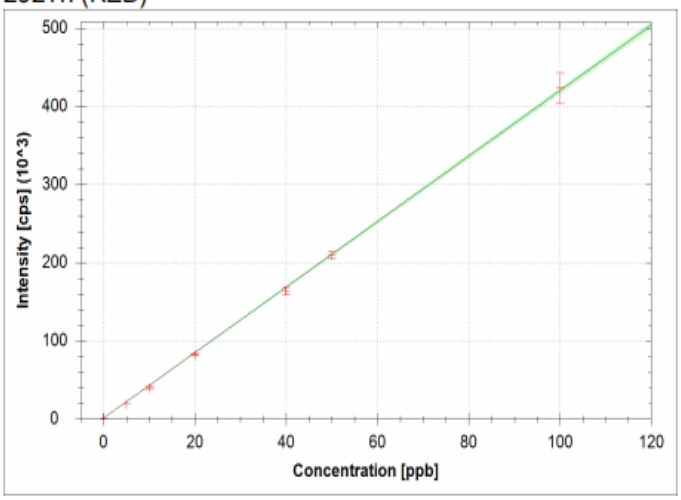
Shows the calibration curves for U and Th radioisotopes (^{232}Th, ^{238}U, ^{228}Th, ^{229}Th, ^{230}Th, ^{232}U, ^{233}U, ^{234}U, ^{235}U and ^{236}U) using multi standards.

232Th (STD)



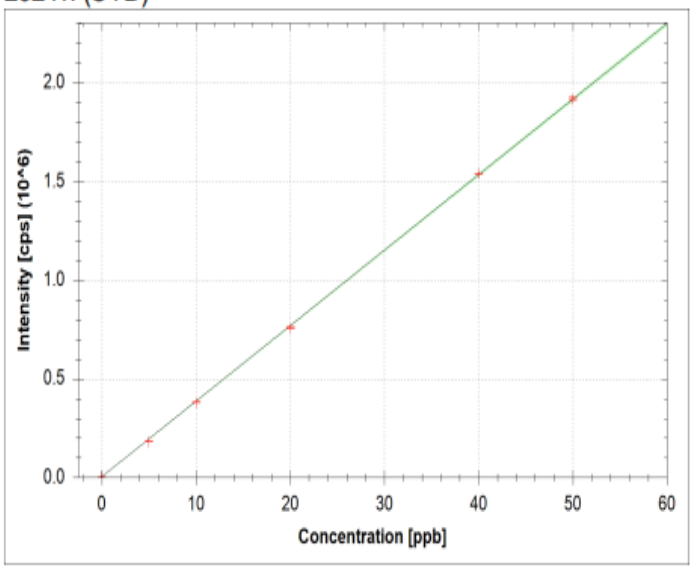
f(x) = 2709.6117*x + 890.9389
R^2 = 0.9993
BEC = 0.329 ppb
LoD = 0.0303 ppb

232Th (KED)



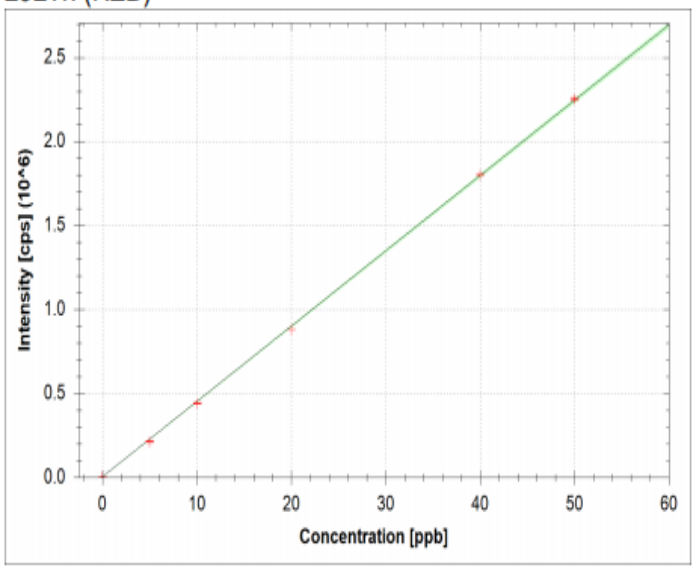
f(x) = 4189.2912*x + 1343.9485
R^2 = 0.9996
BEC = 0.321 ppb
LoD = 0.0350 ppb

232Th (STD)



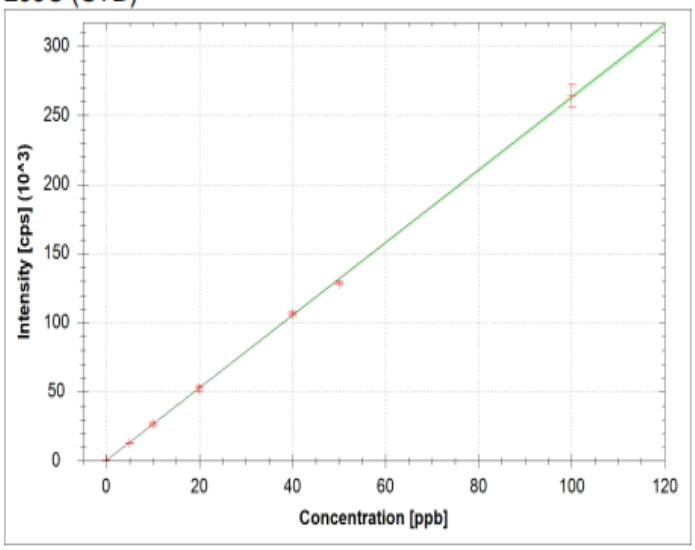
f(x) = 38262.8974*x + 4660.5421
R^2 = 0.9999
BEC = 0.122 ppb
LoD = 0.0014 ppb

232Th (KED)



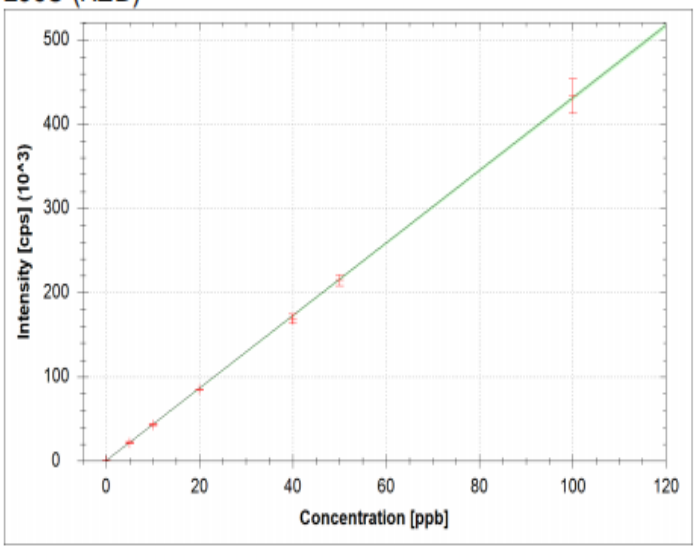
f(x) = 44809.4259*x + 5168.2661
R^2 = 0.9998
BEC = 0.115 ppb
LoD = 0.0043 ppb

238U (STD)



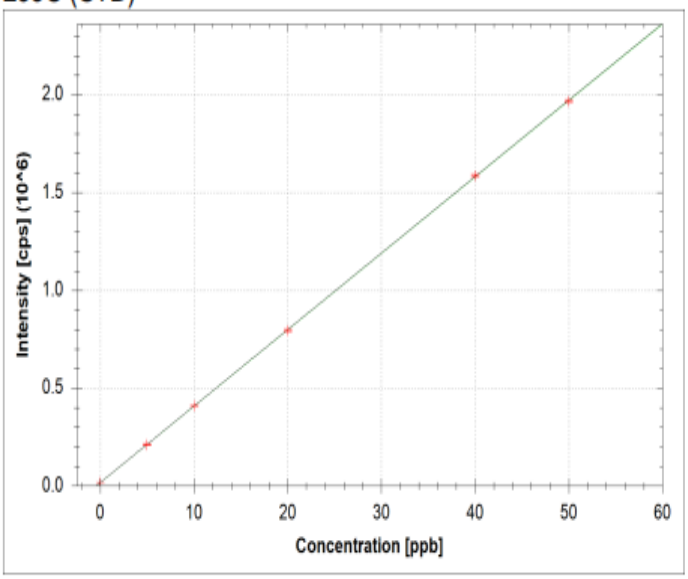
f(x) = 2628.0896*x + 294.9451
R^2 = 0.9997
BEC = 0.112 ppb
LoD = 0.0164 ppb

238U (KED)



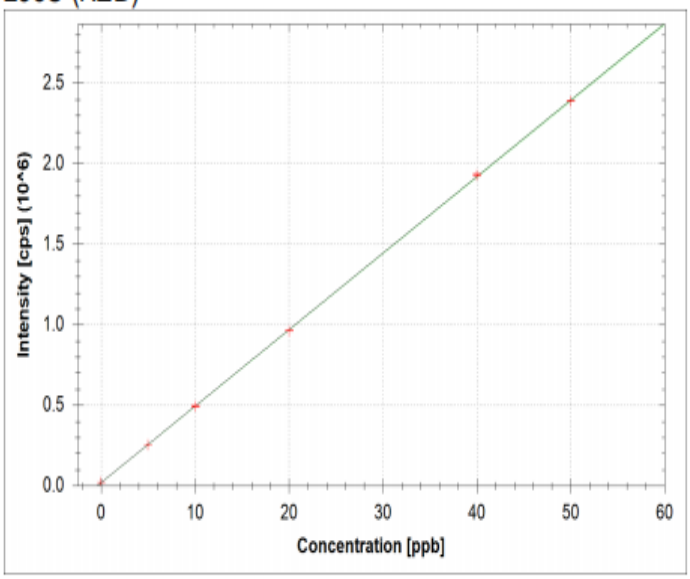
f(x) = 4306.4122*x + 459.3102
R^2 = 0.9998
BEC = 0.107 ppb
LoD = 0.0146 ppb

238U (STD)



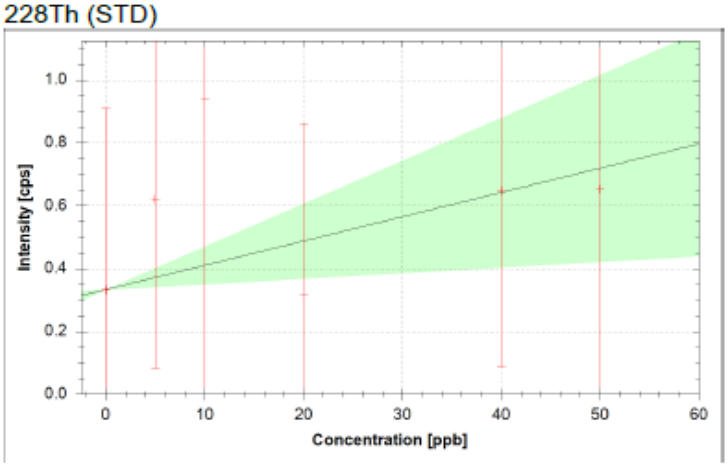
f(x) = 39106.8313*x + 16601.9075
R^2 = 1.0000
BEC = 0.425 ppb
LoD = 0.0103 ppb

238U (KED)



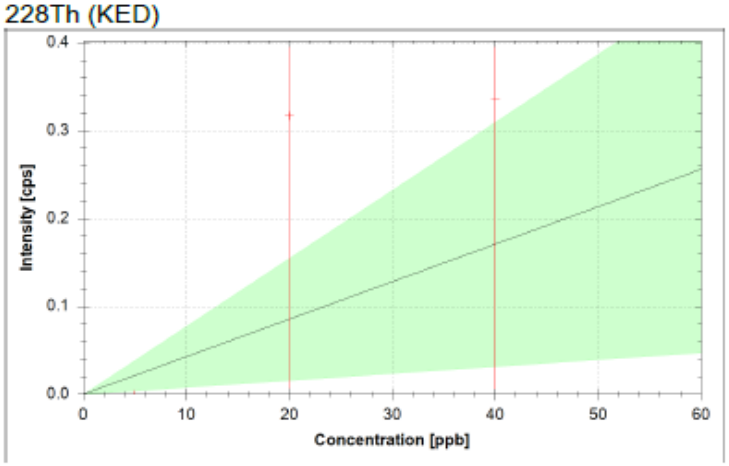
f(x) = 47512.3905*x + 20061.9682
R^2 = 1.0000
BEC = 0.422 ppb
LoD = 0.0085 ppb

228Th (STD)



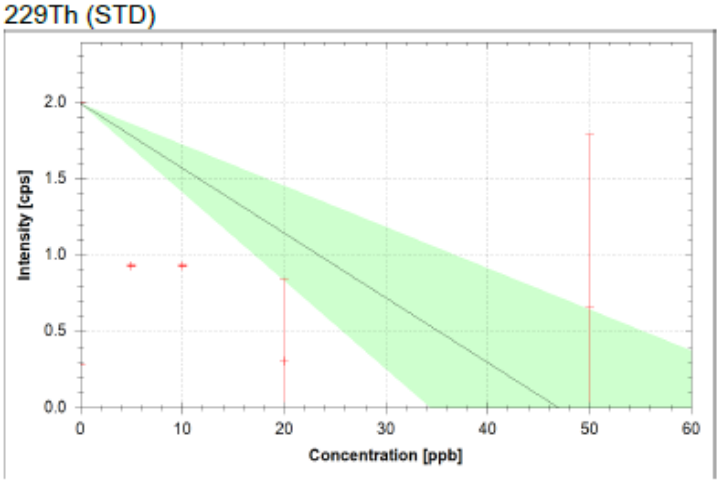
f(x) = 0.0077*x + 0.3329
R^2 = -0.3854
BEC = 43.107 ppb
LoD = 223.9896 ppb

228Th (KED)



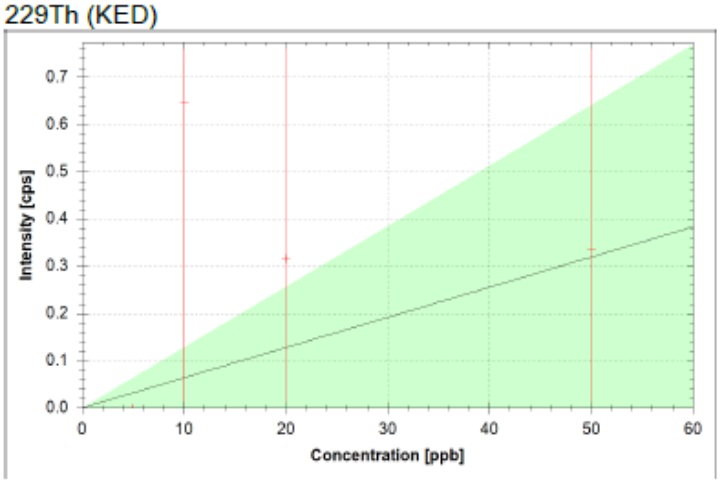
f(x) = 0.0043*x
R^2 = 0.0947
BEC = 0.000 ppb
LoD = 0.0000 ppb

229Th (STD)



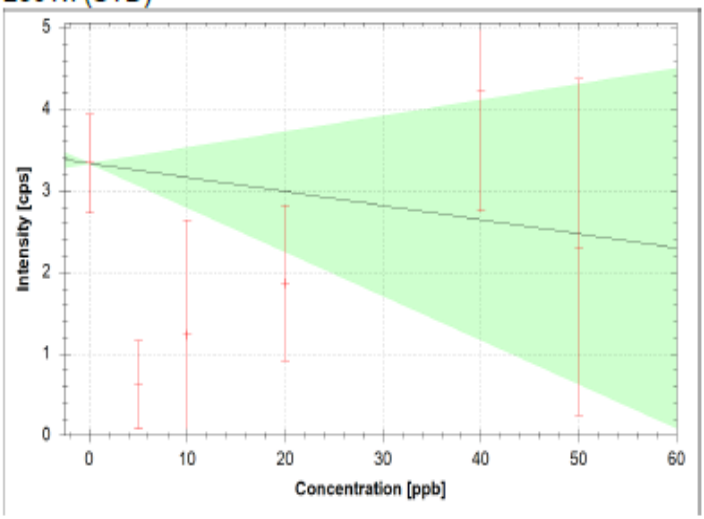
f(x) = -0.0424*x + 1.9932
R² = -0.0712
BEC = -46.992 ppb
LoD = N/A

229Th (KED)



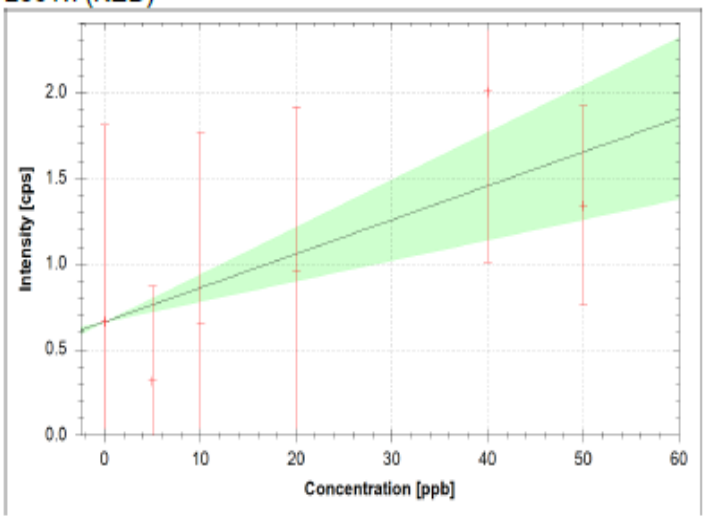
f(x) = 0.0064*x
R² = -0.2627
BEC = 0.000 ppb
LoD = 0.0000 ppb

230Th (STD)



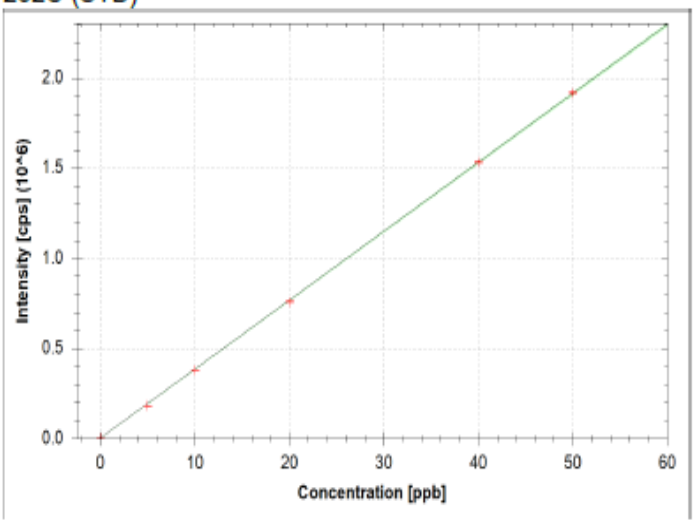
f(x) = -0.0173*x + 3.3362
R² = -0.6206
BEC = -192.706 ppb
LoD = N/A

230Th (KED)



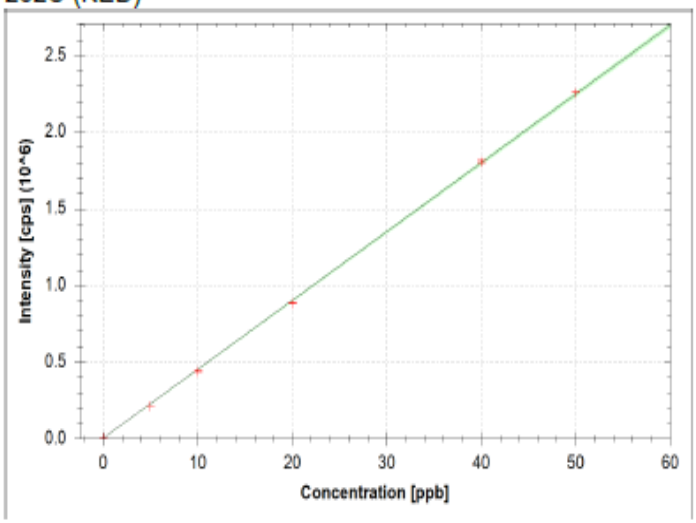
f(x) = 0.0198*x + 0.6623
R² = 0.6433
BEC = 33.454 ppb
LoD = 173.8339 ppb

232U (STD)



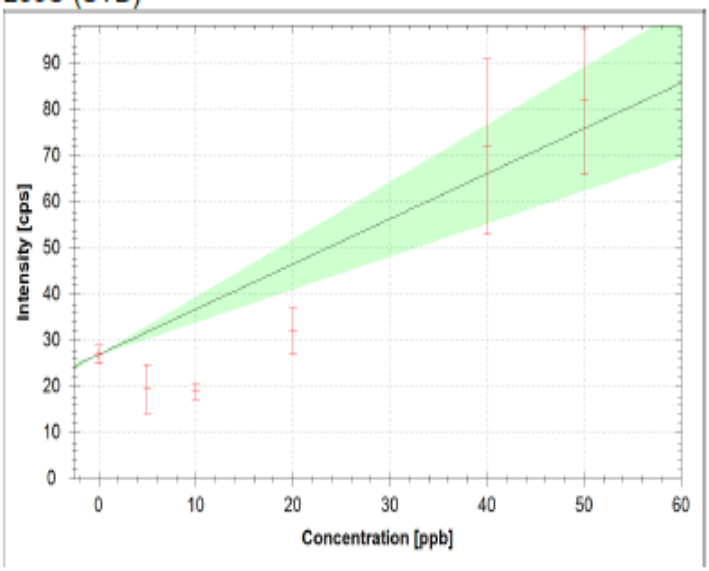
f(x) = 38206.5391*x + 4663.7137
R^2 = 0.9999
BEC = 0.122 ppb
LoD = 0.0025 ppb

232U (KED)



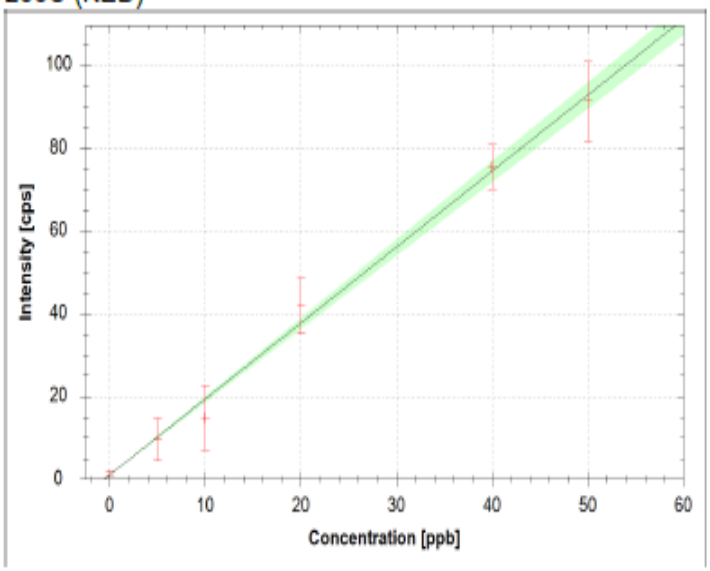
f(x) = 44839.2710*x + 5251.1345
R^2 = 0.9998
BEC = 0.117 ppb
LoD = 0.0059 ppb

233U (STD)



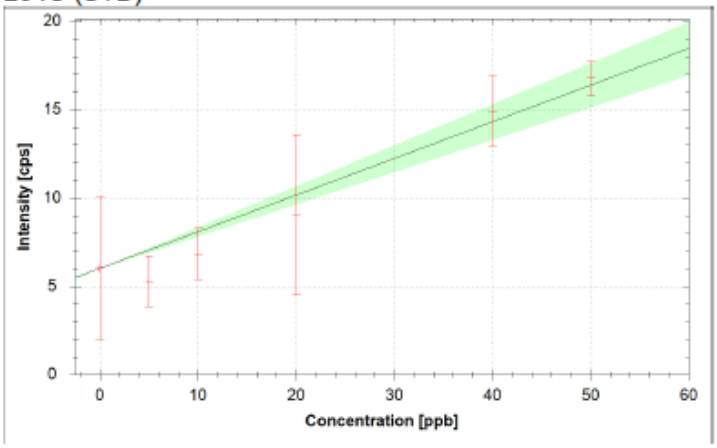
f(x) = 0.9800*x + 27.0093
R^2 = 0.8047
BEC = 27.560 ppb
LoD = 5.9083 ppb

233U (KED)



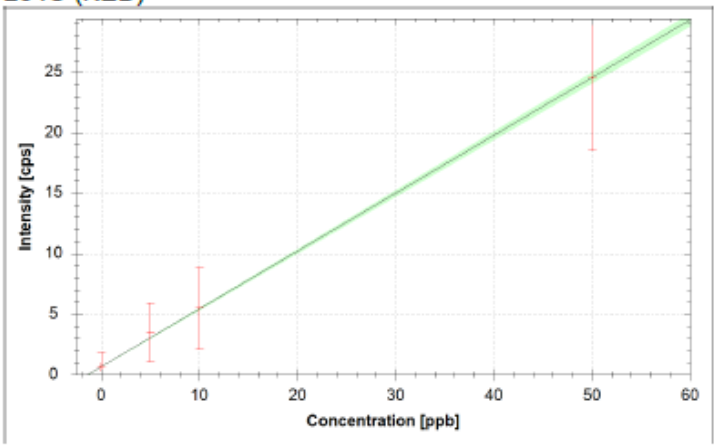
f(x) = 1.8335*x + 1.0023
R^2 = 0.9943
BEC = 0.547 ppb
LoD = 1.6369 ppb

234U (STD)



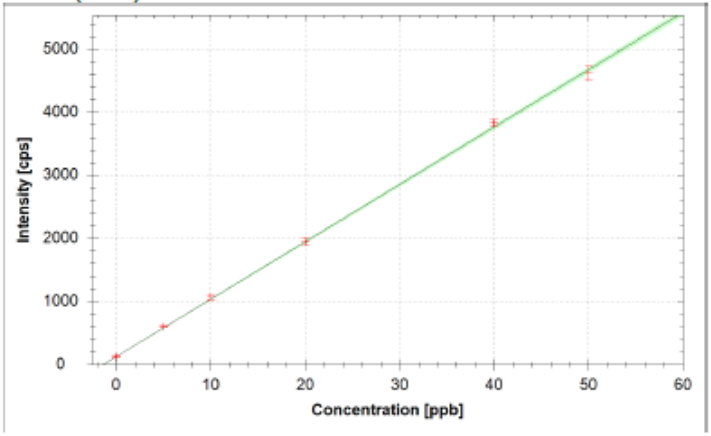
f(x) = 0.2073*x + 6.0202
R² = 0.9452
BEC = 29.034 ppb
LoD = 58.5623 ppb

234U (KED)



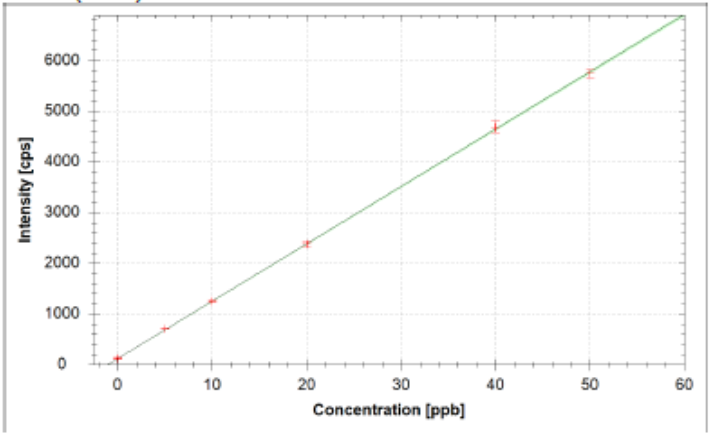
f(x) = 0.4778*x + 0.6670
R² = 0.9994
BEC = 1.396 ppb
LoD = 7.2534 ppb

235U (STD)



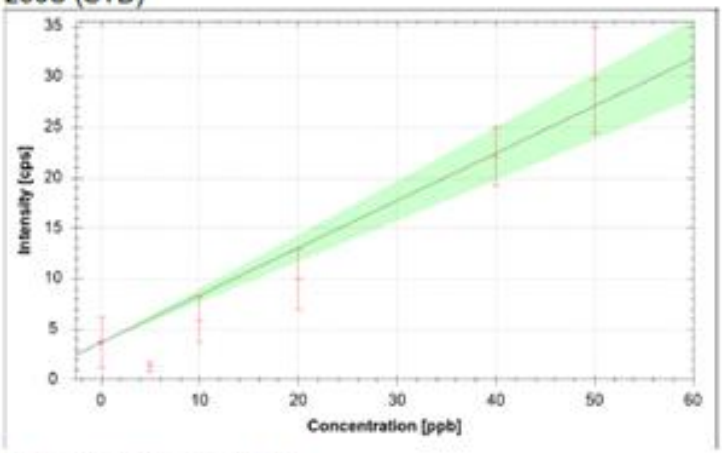
f(x) = 90.8798*x + 129.3299
R² = 0.9994
BEC = 1.423 ppb
LoD = 0.8264 ppb

235U (KED)



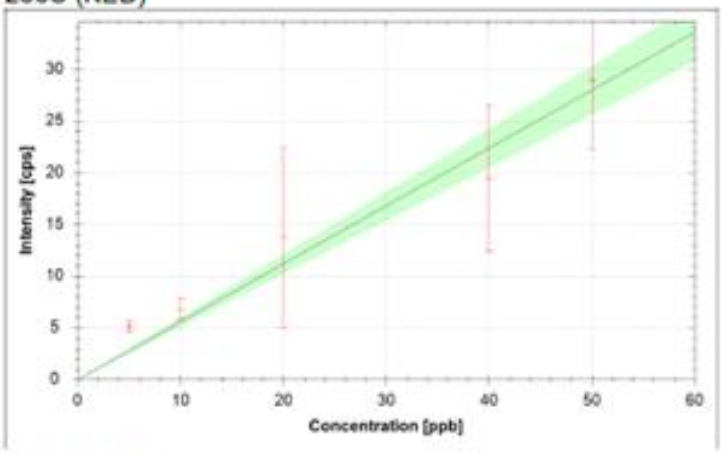
f(x) = 113.1416*x + 120.7065
R² = 0.9999
BEC = 1.067 ppb
LoD = 0.3900 ppb

236U (STD)



f(x) = 0.4682*x + 3.6791
R² = 0.9296
BEC = 7.857 ppb
LoD = 16.2904 ppb

236U (KED)



f(x) = 0.5595*x
R² = 0.9594
BEC = 0.000 ppb
LoD = 0.0000 ppb

Appendix B:

Table of a 10 mL GXR-6 separation data using 4 M HCl and Milli-Q water eluents.

AmberChrom resin 1x8 50-100 mesh 4 M HCl				
Sample volume	**10 mL GXR-6**			
Initial concentrations			**^{232}Th (ppm)**	**^{238}U (ppm)**
GXR-6			**5.54**	**1.60**
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	0.58	0.46	0.01
	2	0.58	2.82	0.52
	3	0.59	2.11	0.00
	4	0.64	1.87	0.27
	5	0.71	2.21	0.35
	6	0.74	1.13	1.38
	7	0.79	0.45	0.40
	8	1.00	1.07	0.10
	9	0.92	0.08	0.42
	10	0.86	0.03	0.03
	11	0.70	0.59	0.46
	12	0.63	0.07	0.88
	13	0.70	0.90	0.52
Milli-Q water	14	0.49	0.13	-0.06
	15	0.50	-0.11	0.44
	16	0.51	-0.11	2.42
	17	0.54	-0.16	0.94
	18	0.72	-0.13	0.25
	19	0.95	-0.01	-0.02
	20	1.12	-0.11	1.65
	21	1.37	-0.11	0.94
	22	1.47	-0.16	0.59
	23	1.56	0.82	0.25
	24	1.63	-0.13	-0.02

Appendix C:

Table of a 15 mL GXR-6 separation data using 4 M HCl and Milli-Q water eluents.

AmberChrom resin 1x8 50-100 mesh	**4 M HCl**			
Sample volume	**15 mL GXR-6**			
Initial concentrations			**^{232}Th (ppm)**	**^{238}U (ppm)**
GXR-6			**5.91**	**1.63**
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	0.38	0.01	0.01
	2	0.38	1.06	-0.33
	3	0.41	2.01	-0.33
	4	0.50	2.69	0.48
	5	0.51	1.35	-0.32
	6	0.48	0.35	-0.32
	7	0.41	0.36	-0.32
	8	0.41	0.52	0.37
	9	0.39	0.06	-0.35
	10	0.39	0.08	-0.18
	11	0.39	0.04	-0.35
	12	0.39	0.07	-0.30
Milli-Q water	13	0.39	-0.01	-0.36
	14	0.39	-0.02	-0.36
	15	0.46	-0.02	-0.36
	16	0.47	-0.02	-0.34
	17	0.48	-0.03	-0.36
	18	0.59	-0.02	-0.20
	19	0.90	-0.02	1.07
	20	1.15	0.00	0.56
	21	1.25	0.00	0.34
	22	1.33	0.00	0.17
	23	1.42	0.00	0.06
	24	1.49	0.00	0.01

Appendix D:

Table of an 18 mL GXR-6 separation data using 4 M HCl and Milli-Q water eluents.

AmberChrom resin 1x8 50-100 mesh	**4 M HCl**			
Sample volume	**18 mL GXR-6**			
Initial concentrations			**^{232}Th (ppm)**	**^{238}U (ppm)**
GXR-6			**5.40**	**1.55**
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	0.45		-0.04
	2	0.46	1.43	-0.03
	3	0.54	3.15	-0.05
	4	0.65	3.29	0.07
	5	0.65	2.81	0.09
	6	0.65	0.88	0.01
	7	0.59	0.41	0.03
	8	0.57	0.73	-0.08
	9	0.56	0.14	0.00
	10	0.55	0.14	0.08
	11	0.53	0.19	-0.04
	12	0.53	0.09	0.28
Milli-Q water	13	0.53	0.29	-0.09
	14	0.54	0.02	-0.09
	15	0.55	0.00	-0.08
	16	0.55	0.05	-0.08
	17	0.58	0.02	-0.03
	18	0.75	0.00	3.98
	19	1.15	-0.01	6.15
	20	1.33	0.00	1.82
	21	1.41	-0.01	0.81
	22	1.50	-0.03	0.39
	23	1.56	-0.03	0.15
	24	1.72	-0.05	0.02

Appendix E:

Table of a 20 mL GXR-6 separation data using 4 M HCl and Milli-Q water eluents.

AmberChrom resin 1x8 50-100 mesh	**4 M HCl**			
Sample volume	**20 mL GXR-6**			
Initial concentrations			**^{232}Th (ppm)**	**^{238}U (ppm)**
GXR-6			**5.30**	**1.55**
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	0.31	-0.20	-0.05
	2	0.32	1.64	-0.05
	3	0.36	3.79	-0.04
	4	0.46	4.68	-0.05
	5	0.64	2.42	0.01
	6	0.53	0.65	-0.03
	7	0.46	0.13	0.00
	8	0.39	-0.08	-0.05
	9	0.41	-0.11	-0.04
	10	0.41	-0.07	-0.04
	11	0.39	-0.12	-0.05
	12	0.38	-0.18	-0.05
Milli-Q water	13	0.38	-0.14	-0.01
	14	0.38	-0.14	-0.01
	15	0.37	-0.15	-0.01
	16	0.37	-0.18	-0.07
	17	0.55	-0.13	3.85
	18	1.19	-0.16	1.90
	19	1.29	-0.18	0.31
	20	1.36	-0.18	0.06
	21	1.40	-0.18	0.00
	22	1.46	-0.18	-0.01
	23	1.54	-0.19	-0.02
	24	1.62	-0.19	-0.02

Appendix F:

Table of a 20 mL GXR-6 separation data using 1 M HCl and Milli-Q water eluents.

AmberChrom resin 1x8 50-100 mesh 1 M HCl				
Sample volume	**20 mL GXR-6**			
Initial concentrations			**^{232}Th (ppm)**	**^{238}U (ppm)**
GXR-6			**5.22**	**1.51**
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	0.99	-0.55	-0.13
	2	1.00	1.88	0.09
	3	0.90	2.95	0.08
	4	0.73	2.92	0.07
	5	0.69	2.60	0.27
	6	0.69	0.55	0.54
	7	0.71	0.29	0.77
	8	0.82	-0.08	0.53
	9	1.02	-0.41	0.20
	10	1.02	-0.44	0.04
	11	1.03	-0.49	-0.03
	12	1.06	-0.50	-0.09
Milli-Q water	13	1.07	-0.47	-0.12
	14	1.07	-0.52	-0.15
	15	1.08	-0.51	-0.16
	16	1.08	-0.37	0.02
	17	1.14	-0.49	-0.17
	18	1.33	-0.50	-0.17
	19	1.78	-0.54	-0.18
	20	1.78	-0.46	-0.17
	21	2.14	-0.49	-0.18
	22	2.23	-0.52	-0.18
	23	2.30	-0.55	-0.18
	24	2.52	-0.54	-0.18

Appendix G:

Table of a 20 mL GXR-6 separation data using 2 M HCl and Milli-Q water eluents.

AmberChrom resin 1x8 50-100 mesh 2 M HCl				
Sample volume	**20 mL GXR-6**			
Initial concentrations			**^{232}Th (ppm)**	**^{238}U (ppm)**
GXR-6			**5.23**	**1.58**
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	0.42	0.00	0.00
	2	0.42	2.40	-0.02
	3	0.49	3.43	-0.01
	4	0.68	3.73	0.23
	5	0.91	2.48	0.49
	6	1.20	0.66	0.30
	7	1.13	0.34	0.10
	8	1.04	0.16	0.07
	9	0.82	0.03	0.05
	10	0.71	-0.08	0.04
	11	0.68	-0.01	0.04
	12	0.61	0.05	0.08
Milli-Q water	13	0.62	-0.14	0.05
	14	0.63	-0.13	0.33
	15	0.60	-0.17	0.09
	16	0.61	-0.09	0.16
	17	0.63	0.00	0.28
	18	1.31	-0.17	1.12
	19	1.41	-0.15	0.54
	20	1.58	-0.20	0.09
	21	1.72	-0.21	0.02
	22	1.87	-0.14	-0.01
	23	1.83	-0.15	-0.03
	24	2.00	-0.22	-0.05

Appendix H:

Table of a 20 mL GXR-6 separation data using 3 M HCl and Milli-Q water eluents.

AmberChrom resin 1x8 50-100 mesh 3 M HCl				
Sample volume	**20 mL GXR-6**			
Initial concentrations			**^{232}Th (ppm)**	**^{238}U (ppm)**
GXR-6			**5.23**	**1.58**
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	0.49	0.08	-0.04
	2	0.50	0.50	-0.04
	3	0.50	2.31	-0.04
	4	0.51	2.95	-0.04
	5	0.61	3.61	0.05
	6	1.07	0.65	0.15
	7	0.99	0.19	-0.01
	8	0.73	0.13	-0.02
	9	0.73	0.09	-0.02
	10	0.66	0.05	0.00
	11	0.67	0.00	0.00
	12	0.67	0.04	-0.02
Milli-Q water	13	0.68	0.02	-0.03
	14	0.67	0.02	-0.03
	15	0.65	0.02	-0.02
	16	0.67	0.02	-0.02
	17	0.64	0.02	0.02
	18	0.71	0.03	1.58
	19	1.05	0.02	2.02
	20	1.36	0.01	0.51
	21	1.43	0.00	0.19
	22	1.56	0.08	0.05
	23	1.66	0.04	-0.02
	24	1.77	-0.01	-0.03

Appendix I:

Table of a 20 mL GXR-6 separation data using 8 M HCl and Milli-Q water eluents.

AmberChrom resin 1x8 50-100 mesh	**8 M HCl**		
Sample volume	**20 mL GXR-6**		
Initial concentrations		**^{232}Th (ppm)**	**^{238}U (ppm)**
GXR-6		**5.30**	**1.55**
Eluent	**Sample fractions**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	0.02	
	2	1.59	-0.05
	3	3.21	0.01
	4	3.94	0.01
	5	2.50	0.01
	6	1.22	0.02
	7	0.62	0.01
	8	0.31	0.01
	9	0.21	0.01
	10	0.16	0.01
	11	0.12	0.01
	12	0.10	0.01
Milli-Q water	13	0.09	0.01
	14	0.08	0.01
	15	0.08	0.01
	16	0.06	0.01
	17	0.06	0.01
	18	0.06	2.09
	19	0.06	2.43
	20	0.06	0.38
	21	0.05	0.13
	22	0.05	0.05
	23	0.05	0.03
	24	0.05	0.02

Appendix J:

Table of a 20 mL GXR-6 separation data at 0-minute contact time.

AmberChrom resin 1x8 50-100 mesh	**4 M HCl**		
Sample volume	**20 mL GXR-6**		
Initial concentrations		**^{232}Th (ppm)**	**^{238}U (ppm)**
GXR-6		**5.26**	**1.60**
Eluent	**Sample fractions**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	0.03	-0.05
	2	2.68	-0.06
	3	3.55	-0.06
	4	3.85	-0.06
	5	1.88	0.05
	6	0.55	-0.03
	7	0.30	-0.05
	8	0.16	-0.06
	9	0.08	-0.06
	10	0.02	-0.06
	11	-0.02	-0.06
	12	-0.02	-0.06
Milli-Q water	13	-0.10	-0.07
	14	-0.13	-0.07
	15	-0.13	-0.06
	16	-0.15	-0.07
	17	-0.16	-0.07
	18	-0.17	2.84
	19	-0.18	1.77
	20	-0.19	0.34
	21	-0.19	0.07
	22	-0.19	-0.02
	23	-0.19	-0.05
	24	-0.19	-0.06

Appendix K:

Table of a 20 mL GXR-6 separation data at 10-minute contact time.

AmberChrom resin 1x8 50-100 mesh	**4 M HCl**		
Sample volume	**20 mL GXR-6**		
Initial concentrations		**^{232}Th (ppm)**	**^{238}U (ppm)**
GXR-6		**5.28**	**1.50**
Eluent	**Sample fractions**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	0.01	0.09
	2	3.17	0.01
	3	3.58	-0.04
	4	0.93	-0.06
	5	0.22	-0.06
	6	0.13	0.04
	7	0.11	0.01
	8	0.07	-0.01
	9	0.07	-0.06
	10	0.08	-0.06
	11	0.03	-0.06
	12	0.03	-0.06
Milli-Q water	13	0.02	-0.05
	14	0.03	-0.06
	15	0.01	-0.07
	16	0.00	-0.06
	17	0.00	-0.07
	18	-0.01	2.93
	19	0.03	0.94
	20	0.00	0.16
	21	-0.01	-0.01
	22	0.00	-0.05
	23	0.00	-0.07
	24	-0.01	-0.07

Appendix L:

Table of a 20 mL GXR-6 separation data at 30-minutes contact time.

AmberChrom resin 1x8 50-100 mesh	**4 M HCl**		
Sample volume	**20 mL GXR-6**		
Initial concentrations		**^{232}Th (ppm)**	**^{238}U (ppm)**
GRX-6		**5.28**	**1.50**
Eluent	**Sample fractions**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	-0.19	-0.07
	2	1.48	-0.07
	3	2.96	-0.07
	4	3.69	-0.07
	5	3.52	-0.05
	6	0.65	0.03
	7	0.17	-0.05
	8	0.08	-0.06
	9	-0.02	-0.06
	10	-0.05	-0.06
	11	-0.08	-0.06
	12	-0.09	-0.06
Milli-Q water	13	-0.10	-0.06
	14	-0.13	-0.07
	15	-0.15	-0.07
	16	-0.17	-0.07
	17	-0.18	-0.07
	18	-0.17	3.06
	19	-0.18	1.82
	20	-0.19	0.25
	21	-0.19	-0.01
	22	-0.19	-0.05
	23	-0.19	-0.07
	24	-0.19	-0.07

Appendix M:

Table of triplicates data for hot plate acid digestion samples and CRMs for ^{232}Th and ^{238}U.

Sample Id	^{232}Th (ppm)	% RSD	% Recovery for ^{232}Th	^{238}U (ppm)	% RSD	% Recovery for ^{232}Th
GXR-6	5.25	0.49	99.31	1.51	1.10	98.00
GXR-6	5.26			1.51		
GXR-6	5.28			1.53		
OREAS 45e	12.94	0.87	101.24	2.49	1.55	102.21
OREAS 45e	12.97			2.44		
OREAS 45e	13.27			2.47		
Sample 1 (483)	12.61	-	-	61.85	-	-
Sample 1 (483)	12.06	-	-	63.79	-	-
Sample 1 (483)	12.12	-	-	60.58	-	-
Sample 2 (488)	1.10	-	-	4.17	-	-
Sample 2 (488)	1.14	-	-	4.07	-	-
Sample 2 (488)	1.07	-	-	4.07	-	-

Appendix N:

Table showing the highest percent recoveries of ^{232}Th and ^{238}U after separation of each sample and CRMs using the three AmberChrom resins including percent errors

	AmberChrom resin 1x8 50-100 mesh				**AmberChrom resin 1x8 20-50 mesh**				**AmberChrom resin 1x2 50-100 mesh**			
Samples	**^{232}Th (%) Yield**	**^{232}Th (%) Error**	**^{238}U (%) Yield**	**^{238}U (%) Error**	**^{232}Th (%) Yield**	**^{232}Th (%) Error**	**^{238}U (%) Yield**	**^{238}U (%) Error**	**^{232}Th (%) Yield**	**^{232}Th (%) Error**	**^{238}U (%) Yield**	**^{238}U (%) Error**
GXR-6	71.98	28.02	167.88	67.88	69.95	30.05	168.19	68.19	56.39	43.61	198.77	98.77
OREAS 45e	74.91	25.09	111.22	11.22	71.98	28.02	92.14	7.86	60.71	39.29	115.46	15.46
Sample 1(483)	80.05	19.95	87.68	12.32	77.71	22.29	52.92	47.08	58.95	41.05	83.54	16.46
Sample 2(488)	94.22	5.78	98.36	1.64	42.37	57.63	77.59	22.41	28.45	71.55	114.39	14.39

Appendix O:

Table of separation of ^{232}Th from ^{238}U from acid digested GXR-6 by AmberChrom 1x8 50-100 mesh resin.

AmberChrom 1x8 50-100 mesh resin	**4 M HCl**			
Sample volume	**20 mL GXR-6**			
Initial concentrations		**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
GRX-6			5.25	1.52
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	0.19	-0.00	-0.07
	2	0.18	1.86	-0.07
	3	0.32	3.06	-0.07
	4	0.43	3.78	0.03
	5	0.49	2.29	0.06
	6	0.35	1.03	-0.04
	7	0.25	0.31	-0.06
	8	0.25	0.21	-0.07
	9	0.26	0.14	-0.06
	10	0.25	0.09	-0.07
	11	0.26	0.03	-0.07
	12	0.25	0.02	-0.07
Milli-Q water	13	0.27	0.00	-0.07
	14	0.25	0.00	-0.07
	15	0.26	-0.01	-0.07
	16	0.27	-0.01	-0.07
	17	0.24	-0.05	-0.06
	18	0.42	-0.02	2.10
	19	0.93	-0.04	2.55
	20	1.07	-0.08	0.50
	21	1.17	-0.09	0.16
	22	1.25	-0.09	0.04
	23	1.33	-0.09	-0.03
	24	1.42	-0.09	-0.06

Appendix P:

Table of separation of ^{232}Th from ^{238}U from acid digested OREAS 45e by AmberChrom 1x8 50-100 mesh resin.

AmberChrom 1x8 50-100 mesh resin	**4 M HCl**			
Sample volume	**20 mL OREAS 45e**			
Initial concentrations		**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
OREAS 45e			12.94	2.49
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	0.31	0.00	-0.07
	2	0.32	7.18	-0.08
	3	0.43	9.69	-0.07
	4	0.50	9.16	-0.06
	5	0.84	3.01	-0.03
	6	0.96	0.89	-0.06
	7	0.83	0.49	-0.07
	8	0.60	0.36	-0.07
	9	0.39	0.25	-0.07
	10	0.33	0.15	-0.07
	11	0.33	0.07	-0.07
	12	0.29	0.01	-0.06
Milli-Q water	13	0.23	0.00	-0.07
	14	0.24	-0.01	-0.07
	15	0.23	0.03	-0.07
	16	0.24	-0.07	-0.07
	17	0.27	-0.07	-0.03
	18	0.41	-0.05	3.32
	19	0.99	-0.10	3.26
	20	1.17	-0.12	0.74
	21	1.19	-0.12	0.34
	22	1.26	-0.13	0.12
	23	1.32	-0.14	0.01
	24	1.36	-0.14	-0.04

Appendix Q:

Table of separation of ^{232}Th from ^{238}U from acid digested Sample 1 (483) by AmberChrom 1x8 50-100 mesh resin.

AmberChrom 1x8 50-100 mesh resin	**4 M HCl**			
Sample volume	**20 mL Sample 1 (483)**			
Initial concentrations		**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
Sample 1 (483)			12.61	61.85
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	1.20	-0.10	-0.11
	2	1.15	5.48	-0.11
	3	1.20	10.10	1.29
	4	1.35	7.38	54.23
	5	1.53	1.93	43.75
	6	1.35	0.74	2.63
	7	1.20	0.64	1.24
	8	1.16	0.46	0.50
	9	1.15	0.36	0.21
	10	1.16	0.35	0.26
	11	1.14	0.31	0.10
	12	1.15	0.28	0.02
Milli-Q water	13	1.15	0.30	0.02
	14	1.15	0.13	0.00
	15	1.15	0.03	0.01
	16	1.14	-0.05	0.00
	17	1.14	-0.06	0.16
	18	1.27	-0.05	37.33
	19	1.81	-0.09	43.50
	20	2.11	-0.12	8.76
	21	2.16	-0.14	3.45
	22	2.22	-0.14	1.60
	23	2.32	-0.14	0.52
	24	2.38	-0.14	0.21

Appendix R:

Table of separation of ^{232}Th from ^{238}U from acid digested Sample 1 (488) by AmberChrom 1x8 50-100 mesh resin.

AmberChrom 1x8 50-100 mesh resin	**4 M HCl**			
Sample volume	**20 mL Sample 1 (488)**			
Initial concentrations		**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
Sample 1 (488)			1.10	4.17
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	1.10	0.00	-0.09
	2	1.06	0.63	-0.10
	3	1.14	1.04	-0.04
	4	1.22	0.84	2.33
	5	1.41	0.19	4.10
	6	1.31	0.00	0.16
	7	1.13	0.00	-0.05
	8	1.08	-0.01	-0.09
	9	1.08	-0.02	-0.10
	10	1.08	-0.04	-0.10
	11	1.09	-0.05	-0.10
	12	1.07	-0.06	-0.11
Milli-Q water	13	1.08	-0.07	-0.11
	14	1.07	-0.07	-0.11
	15	1.08	-0.08	-0.10
	16	1.09	-0.10	-0.11
	17	1.20	-0.10	-0.10
	18	1.77	-0.08	2.59
	19	2.00	-0.11	3.50
	20	2.03	-0.13	0.49
	21	2.10	-0.13	0.14
	22	2.15	-0.13	-0.02
	23	2.17	-0.14	-0.08
	24	2.20	-0.13	-0.09

Appendix S:

Table of separation of ^{232}Th from ^{238}U from acid digested GXR-6 by AmberChrom 1x8 20-50 mesh resin.

AmberChrom 1x8 20-50 mesh resin	**4 M HCl**			
Sample volume	**20 mL GXR-6**			
Initial concentrations		**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
GRX-6			5.26	1.51
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	1.11	-0.18	-0.11
	2	1.14	2.23	-0.11
	3	1.22	3.25	-0.10
	4	1.26	3.68	-0.03
	5	1.36	3.00	0.14
	6	1.40	0.82	0.14
	7	1.36	0.05	0.00
	8	1.32	-0.11	-0.06
	9	1.25	-0.17	-0.09
	10	1.25	-0.19	-0.09
	11	1.25	-0.21	-0.10
	12	1.25	-0.22	-0.09
Milli-Q water	13	1.22	-0.23	-0.09
	14	1.22	-0.23	-0.10
	15	1.21	-0.18	-0.09
	16	1.21	-0.09	-0.09
	17	1.23	-0.26	-0.07
	18	1.32	-0.29	0.93
	19	1.86	-0.29	2.53
	20	2.26	-0.32	0.22
	21	2.33	-0.33	0.04
	22	2.41	-0.33	-0.02
	23	2.47	-0.34	-0.06
	24	2.54	-0.33	-0.08

Appendix T:

Table of separation of ^{232}Th from ^{238}U from acid digested OREAS 45e by AmberChrom 1x8 20-50 mesh resin.

AmberChrom 1x8 20-50 mesh resin	**4 M HCl**			
Sample volume	**20 mL OREAS 45e**			
Initial concentrations		**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
OREAS 45e			12.97	2.44
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	1.09	-0.16	-0.07
	2	1.1	2.80	-0.07
	3	1.11	6.75	-0.06
	4	1.15	8.83	-0.01
	5	1.79	9.34	0.25
	6	1.87	3.99	0.62
	7	1.77	1.32	0.26
	8	1.75	0.90	0.05
	9	1.67	0.67	-0.02
	10	1.59	0.50	-0.04
	11	1.52	0.34	-0.05
	12	1.43	0.26	-0.05
Milli-Q water	13	1.32	0.24	-0.05
	14	1.31	0.08	-0.05
	15	1.29	0.07	-0.04
	16	1.29	0.00	-0.04
	17	1.3	-0.19	-0.03
	18	1.34	-0.24	0.80
	19	1.69	-0.27	2.24
	20	2.15	-0.29	0.40
	21	2.22	-0.29	0.13
	22	2.29	-0.30	0.02
	23	2.34	-0.30	-0.01
	24	2.38	-0.30	-0.04

Appendix U:

Table of separation of ^{232}Th from ^{238}U from acid digested sample 1(483) by AmberChrom 1x8 20-50 mesh resin.

AmberChrom 1x8 20-50 mesh resin	**4 M HCl**			
Sample volume	**20 mL Sample 1(483)**			
Initial concentrations		**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
Sample 1(483)			12.06	63.79
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	1.12	-0.27	-0.06
	2	1.12	3.80	-0.02
	3	1.15	9.37	1.63
	4	1.21	7.58	21.95
	5	1.32	2.30	29.77
	6	1.29	0.87	12.37
	7	1.24	0.65	4.29
	8	1.19	0.52	1.54
	9	1.18	0.41	0.97
	10	1.17	0.35	0.79
	11	1.17	0.35	0.69
	12	1.16	0.26	0.45
Milli-Q water	13	1.17	0.09	0.40
	14	1.17	0.10	0.39
	15	1.17	0.06	0.41
	16	1.16	-0.09	0.63
	17	1.21	-0.23	3.97
	18	1.33	-0.24	33.76
	19	1.68	-0.26	30.96
	20	1.99	-0.28	7.71
	21	2.05	-0.29	3.96
	22	2.15	-0.30	2.37
	23	2.23	-0.30	1.42
	24	2.31	-0.30	0.54

Appendix V:

Table of separation of ^{232}Th from ^{238}U from acid digested sample 2(488) by AmberChrom 1x8 20-50 mesh resin.

AmberChrom 1x8 20-50 mesh resin	**4 M HCl**			
Sample volume	**20 mL Sample 2(488)**			
Initial concentrations		**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
Sample 2(488)			1.14	4.07
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	1.19	-0.18	-0.10
	2	1.19	-0.01	-0.10
	3	1.19	0.28	-0.07
	4	1.23	0.48	0.10
	5	1.29	0.33	0.79
	6	1.35	-0.09	1.13
	7	1.32	-0.22	0.57
	8	1.27	-0.24	0.20
	9	1.15	-0.25	0.03
	10	1.13	-0.25	-0.02
	11	1.1	-0.25	-0.05
	12	1.08	-0.27	-0.06
Milli-Q water	13	1.09	-0.31	-0.06
	14	1.09	-0.31	-0.06
	15	1.06	-0.30	-0.06
	16	1.07	-0.29	-0.06
	17	1.08	-0.32	-0.02
	18	1.13	-0.32	0.49
	19	1.3	-0.33	3.16
	20	1.74	-0.33	2.39
	21	2.06	-0.33	0.53
	22	2.13	-0.33	0.46
	23	2.21	-0.34	0.17
	24	2.39	-0.34	-0.03

Appendix W:

Table of separation of ^{232}Th from ^{238}U from acid digested GXR-6 by AmberChrom 1x2 50-100 mesh resin.

AmberChrom 1x2 50-100 mesh resin	**4 M HCl**			
Sample volume	**20 mL GXR-6**			
Initial concentrations		**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
GRX-6			5.28	1.53
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	1.18	-0.31	-0.11
	2	1.18	0.73	-0.11
	3	1.21	2.21	-0.11
	4	1.32	2.98	-0.10
	5	1.41	1.93	0.10
	6	1.47	0.93	0.18
	7	1.38	0.42	0.01
	8	1.27	0.19	-0.08
	9	1.24	0.05	-0.09
	10	1.23	-0.01	-0.10
	11	1.23	-0.11	-0.10
	12	1.22	-0.20	-0.10
Milli-Q water	13	1.19	-0.25	-0.09
	14	1.2	-0.26	-0.09
	15	1.2	-0.27	-0.09
	16	1.2	-0.28	-0.09
	17	1.19	-0.29	-0.08
	18	1.2	-0.31	-0.05
	19	1.36	-0.32	3.04
	20	1.94	-0.33	1.95
	21	2.03	-0.34	-0.07
	22	2.08	-0.34	-0.10
	23	2.14	-0.34	-0.11
	24	2.21	-0.34	-0.11

Appendix X:

Table of separation of ^{232}Th from ^{238}U from acid digested OREAS 45e by AmberChrom 1x2 50-100 mesh resin.

AmberChrom 1x2 50-100 mesh resin	**4 M HCl**			
Sample volume	**OREAS 45e**			
Initial concentrations		**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
OREAS 45e			13.15	2.42
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	1.15	0.06	-0.04
	2	1.16	2.24	-0.05
	3	1.17	5.65	-0.05
	4	1.21	7.57	-0.05
	5	1.29	7.98	0.05
	6	1.41	6.20	0.40
	7	1.52	3.31	0.52
	8	1.77	1.35	0.10
	9	1.64	0.73	-0.02
	10	1.47	0.49	-0.05
	11	1.35	0.41	-0.04
	12	1.34	0.34	-0.04
Milli-Q water	13	1.31	0.26	-0.04
	14	1.29	0.22	-0.03
	15	1.29	0.15	-0.03
	16	1.24	0.03	-0.02
	17	1.25	-0.10	-0.03
	18	1.29	-0.18	0.08
	19	1.41	-0.22	2.12
	20	1.71	-0.28	2.79
	21	2.07	-0.30	0.03
	22	2.13	-0.30	-0.06
	23	2.21	-0.30	-0.07
	24	2.32	-0.31	-0.07

Appendix Y:

Table of separation of ^{232}Th from ^{238}U from acid digested sample 1(483) by AmberChrom 1x2 50-100 mesh resin.

AmberChrom 1x2 50-100 mesh resin	**4 M HCl**			
Sample volume	**20 mL Sample 1(483)**			
Initial concentrations		**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
Sample 1(483)			12.12	60.58
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	1.18	-0.33	-0.11
	2	1.18	0.50	-0.11
	3	1.19	3.58	-0.11
	4	1.25	6.51	0.01
	5	1.32	7.14	5.89
	6	1.44	4.89	30.83
	7	1.53	2.60	29.80
	8	1.39	1.01	5.04
	9	1.29	0.68	1.26
	10	1.29	0.53	0.52
	11	1.30	0.37	0.39
	12	1.31	0.26	0.37
Milli-Q water	13	1.29	0.13	0.41
	14	1.29	0.07	0.52
	15	1.28	0.02	0.60
	16	1.28	-0.04	0.67
	17	1.29	-0.16	0.71
	18	1.28	-0.24	3.09
	19	1.34	-0.28	50.61
	20	1.45	-0.32	48.21
	21	1.77	-0.33	0.94
	22	1.99	-0.33	0.03
	23	2.20	-0.34	-0.05
	24	2.59	-0.33	-0.10

Appendix Z:

Table of separation of ^{232}Th from ^{238}U from acid digested sample 2(488) by AmberChrom 1x2 50-100 mesh resin.

AmberChrom 1x2 50-100 mesh resin	**4 M HCl**			
Sample volume	**20 mL Sample 2(488)**			
Initial concentrations		**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
Sample 2(488)			1.07	4.07
Eluent	**Sample fractions**	**pH**	**^{232}Th (ppm)**	**^{238}U (ppm)**
4 M HCl	1	1.22	-0.31	-0.11
	2	1.23	-0.12	-0.11
	3	1.23	0.15	-0.10
	4	1.29	0.30	-0.04
	5	1.37	0.29	0.90
	6	1.47	0.09	2.60
	7	1.48	-0.15	1.09
	8	1.29	-0.22	0.12
	9	1.22	-0.25	-0.03
	10	1.22	-0.27	-0.07
	11	1.2	-0.29	-0.07
	12	1.2	-0.30	-0.07
Milli-Q water	13	1.18	-0.30	-0.06
	14	1.18	-0.31	-0.06
	15	1.18	-0.31	-0.06
	16	1.18	-0.31	-0.03
	17	1.17	-0.32	-0.04
	18	1.19	-0.33	0.17
	19	1.33	-0.33	4.66
	20	2.05	-0.34	3.12
	21	2.2	-0.34	0.03
	22	2.23	-0.34	-0.10
	23	2.25	-0.34	-0.10
	24	2.34	-0.34	-0.10

Appendix AA:

Table of separation of ^{232}Th from ^{238}U from acid digested GXR-6 by AmberChrom 1x8 50-100 mesh resin using 8 M HCl eluent and Milli-Q water.

AmberChrom resin 1x8 50-100 mesh	**8 M HCl**		
Sample volume	**20 mL GXR-6**		
Initial concentrations		**^{232}Th (ppm)**	**^{238}U (ppm)**
GXR-6		5.32	1.51
Eluent	**Sample fractions**	**^{232}Th (ppm)**	**^{238}U (ppm)**
8 M HCl	1	0.00	0.00
	2	2.36	-0.08
	3	4.00	-0.08
	4	1.51	0.00
	5	0.34	0.02
	6	0.15	-0.07
	7	0.07	-0.08
	8	-0.04	-0.09
	9	-0.13	-0.09
	10	-0.17	-0.09
	11	-0.20	-0.09
	12	-0.28	-0.09
Milli-Q water	13	-0.30	-0.09
	14	-0.30	-0.09
	15	-0.31	-0.09
	16	-0.33	-0.09
	17	-0.34	-0.05
	18	-0.34	2.40
	19	-0.35	1.66
	20	-0.36	0.31
	21	-0.36	0.11
	22	-0.36	0.04
	23	-0.37	-0.03
	24	-0.37	-0.06

Appendix BB:

Table of separation of ^{232}Th from ^{238}U from acid digested OREAS 45e by AmberChrom 1x8 50-100 mesh resin using 8 M HCl eluent and Milli-Q water.

AmberChrom resin 1x8 50-100 mesh	**8 M HCl**		
Sample volume	**20 mL OREAS 45e**		
Initial concentrations		**^{232}Th (ppm)**	**^{238}U (ppm)**
OREAS 45e		13.2709	2.4719
Eluent	**Sample fractions**	**^{232}Th (ppm)**	**^{238}U (ppm)**
8 M HCl	1	-0.13	-0.05
	2	6.42	-0.06
	3	10.89	-0.06
	4	5.89	0.36
	5	2.89	0.79
	6	2.52	0.00
	7	1.57	-0.06
	8	0.72	-0.06
	9	0.38	-0.06
	10	0.30	-0.06
	11	0.21	-0.06
	12	0.03	-0.06
Milli-Q water	13	-0.04	-0.05
	14	-0.04	-0.06
	15	-0.06	-0.06
	16	-0.13	-0.06
	17	-0.13	0.14
	18	-0.13	3.37
	19	-0.16	1.34
	20	-0.16	0.42
	21	-0.17	0.20
	22	-0.18	0.09
	23	-0.18	0.01
	24	-0.19	-0.03

Appendix CC:

Table of separation of ^{232}Th from ^{238}U from acid digested Sample 1 (483) by AmberChrom 1x8 50-100 mesh resin using 8 M HCl eluent and Milli-Q water.

AmberChrom resin 1x8 50-100 mesh	**8 M HCl**		
Sample volume	**20 mL Sample 1 (483)**		
Initial concentrations		**^{232}Th (ppm)**	**^{238}U (ppm)**
Sample 1 (483)		12.6110	61.8503
Eluent	**Sample fractions**	**^{232}Th (ppm)**	**^{238}U (ppm)**
8 M HCl	1	0.18	-0.06
	2	5.68	-0.06
	3	7.90	-0.05
	4	3.14	0.86
	5	1.87	1.32
	6	1.42	0.03
	7	0.67	-0.04
	8	0.44	-0.05
	9	0.23	-0.05
	10	0.07	-0.05
	11	0.01	-0.05
	12	-0.05	-0.05
Milli-Q water	13	-0.07	-0.05
	14	-0.09	-0.05
	15	-0.06	-0.05
	16	-0.12	-0.05
	17	-0.14	-0.03
	18	-0.15	70.44
	19	-0.16	93.97
	20	-0.17	16.92
	21	-0.18	4.59
	22	-0.18	1.94
	23	-0.18	0.92
	24	-0.18	0.57

Appendix DD:

Table of separation of ^{232}Th from ^{238}U from acid digested Sample 2 (488) by AmberChrom 1x8 50-100 mesh resin using 8 M HCl eluent and Milli-Q water.

AmberChrom resin 1x8 50-100 mesh	**8 M HCl**		
Sample volume	**20 mL Sample 2 (488)**		
Initial concentrations		**^{232}Th (ppm)**	**^{238}U (ppm)**
Sample 2 (488)		1.1026	4.1720
Eluent	**Sample fractions**	**^{232}Th (ppm)**	**^{238}U (ppm)**
8 M HCl	1	-0.17	-0.06
	2	0.37	-0.03
	3	0.75	-0.05
	4	0.26	1.42
	5	0.08	1.36
	6	-0.02	0.00
	7	-0.03	-0.05
	8	-0.09	-0.06
	9	-0.13	-0.05
	10	-0.14	-0.05
	11	-0.14	-0.06
	12	-0.15	-0.06
Milli-Q water	13	-0.16	-0.05
	14	-0.16	-0.05
	15	-0.16	-0.05
	16	-0.17	-0.05
	17	-0.17	-0.05
	18	-0.17	5.13
	19	-0.18	3.32
	20	-0.18	0.66
	21	-0.1	0.17
	22	-0.19	-0.04
	23	-0.18	-0.03
	24	-0.18	-0.05

Appendix EE:

Thermo Fisher Scientific iCAP Q (ICP-QMS) operating parameters.

Parameters	Conditions
RF power	1400-1550 W
Sampling depth	4.5-5.5 mm
Make Up gas flow (Ar)	0.55-0.75 l/min
Coolant gas flow (Ar)	20 l/min
Auxiliary gas flow (Ar)	1.50 l/min
Nebuliser Flow	1.50 l/min
Plasma cooling water flow	11.60 l/min
Spray chamber temperature	20 °C
Dwell time/mass	10-50 ms
Sampler, skimmer	Ni (with high sensitivity insert)
Nebuliser	PFA MicroFlow ST
Coolant gas flow (Ar)	14 l/min
Auxiliary gas flow (Ar)	0.8 l/min
Isotopes	238U and 232Th