universität wien

DIPLOMARBEIT

„Determination of ^{236}U, ^{238}U and ^{234}U isotopes and the $^{240}Pu/^{239}Pu$ ratio in water samples“

Verfasserin

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angestrebter akademischer Grad

Magistra der Naturwissenschaften (Mag^{a}. rer. nat)

Studienkennzahl lt. Studienblatt:	A 419
Studienrichtung lt. Studienblatt:	Chemie
Betreuerin:	Ao. Univ.-Prof. Mag. Dr. Gabriele Wallner

Wien, Juni 2011

Acknowledgement

This diploma thesis was conducted from September 2010 to May 2011 at the Institute for Inorganic Chemistry of the University of Vienna.

First of all, I would like to thank my supervisor, Ao. Univ.-Prof. Dr. Gabriele Wallner for her guidance and support throughout this whole time.

I am also grateful for the help and advice from Dr. Michaela Srncik, who taught me a lot about the working methods that were required for my analysis.

I would also like to show my gratitude to Dr. Peter Steier, who measured my samples by AMS and allowed me to work in his laboratory. Furthermore, I want to thank both Dr. Peter Steier and Dr. Alfred Priller for collecting my samples.

My thanks also go to my colleagues, Dr. Michaela Srncik, Mag. Gabriela Wallova and Tania Jabbar MSc for the good time and interesting discussions we shared.

This diploma thesis and my studies in general would not have been possible without the support from my mother and therefore, I am deeply grateful and thank her for believing in me and encouraging me.

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Abstract

In the course of this diploma thesis, water samples from rivers and oceans were analyzed regarding their content of ^{234}U and ^{238}U and their $^{236}U/^{238}U$ and $^{240}Pu/^{239}Pu$ ratios.

In the beginning, a suitable method for the separation of uranium and plutonium from large water samples had to be found. For this purpose, three different methods were tested on tap water, mine water and artificial sea water. In those preliminary tests, a ^{232}U spike solution was used and uranium was separated by different resins. Then uranium was co-precipitated with NdF_3 and measured by alpha-spectrometry.

A sample preparation method using $Fe(OH)_3$ co-precipitation proved to be most efficient and was best suited for the handling of sea water samples. Based on this method, two different separation procedures for the combined extraction of uranium and plutonium (using ^{242}Pu spike solution) were tested.

The sample preparation method which was finally chosen consists of separating plutonium by Dowex® 1x8 resin, followed by uranium extraction using UTEVA® resin.

The river and sea water samples were collected from different places around the world. The $^{236}U/^{238}U$ and $^{239}Pu/^{240}Pu$ isotopic ratios were measured by accelerator mass spectrometry (AMS), whereas the ^{234}U and ^{238}U activity concentrations were assessed by alpha-spectrometry.

All samples seem to be affected by the nuclear activity of mankind. The water samples show typical values ascertained for global fallout, with the exception of water from the Irish Sea, which was clearly influenced by the reprocessing plant in Sellafield, UK.

Zusammenfassung

Im Rahmen dieser Diplomarbeit wurden die Isotopenverhältnisse von $^{239}Pu/^{240}Pu$ und $^{236}U/^{238}U$ sowie der Gehalt der Radionuklide ^{234}U und ^{238}U in verschiedenen Gewässern analysiert.

Dafür wurde zuerst eine geeignete Probenvorbereitung gesucht. Zu diesem Zweck wurden drei verschiedene Methoden an Leitungswasser, Wasser aus einem Bergwerk und künstlichem Meerwasser ausprobiert. Dabei wurde ein ^{232}U spike verwendet und verschiedene Harze wurden zur Abtrennung des Urans getestet. Nach einer Mikropräzipitation mit NdF_3 wurde der Gehalt an Uran mittels Alphaspektrometrie bestimmt.

Die Probenvorbereitung, die sich als am besten geeignet für Meerwasserproben erwiesen hat, basiert auf der Mitfällung des Urans mit $Fe(OH)_3$. Diese Methode wurde dann als Ausgangspunkt für zwei weitere Tests verwendet, in denen zwei verschiedene Trenntechniken für Uran und Plutonium (unter Verwendung eines ^{242}Pu spikes) getestet wurden.

Für die gleichzeitige Bestimmung dieser beiden Elemente wurde eine Methode gewählt, bei der Plutonium mit einem Dowex® 1x8 Harz und Uran im Anschluss daran mittels UTEVA® Harz separiert wird.

Die Wasserproben wurden verschiedenen Flüssen und Ozeanen entnommen. Die Isotopenverhältnisse $^{239}Pu/^{240}Pu$ bzw. $^{236}U/^{238}U$ wurden mittels Beschleunigungsmassenspektrometrie (AMS) ermittelt, während Alphaspektrometrie für die Bestimmung der Aktivitätskonzentrationen von ^{234}U und ^{238}U herangezogen wurde.

Bei der Analyse der Ergebnisse wurde festgestellt, dass alle Proben durch die nukleare Aktivität des Menschen der letzten Jahrzehnte beeinflusst waren. Die Isotopenverhältnisse zeigen Werte, wie sie für den globalen Fallout üblich sind, mit Ausnahme der Probe des Wassers aus der Irischen See, welche eindeutig den Einfluss der Wiederaufbearbeitungsanlage in Sellafield zeigt.

1 Introduction

1.1 Preface

Radioactivity was discovered in 1896 when Becquerel found that uranium salts led to the blackening of photographic plates. Both naturally occurring and man-made radio isotopes can be found in nature. Natural radio isotopes are either produced continuously by cosmic radiation (^{3}H, ^{14}C) or exist since the genesis of elements (primordial radionuclides; ^{40}K, ^{232}Th, ^{238}U, ^{235}U). Due to their long half lives, the isotopes ^{232}Th ($1.405 \cdot 10^{10}$ a), ^{238}U ($4.468 \cdot 10^{9}$ a) and ^{235}U ($7.038 \cdot 10^{8}$ a) represent the starting points of the three decay series that have been going on since the nucleogenesis and can still be found in nature. ^{237}Np has a short half-life ($2.144 \cdot 10^{6}$ a) compared to the age of the earth (about $5 \cdot 10^{9}$ a) and therefore its decay series is extinct in nature [1].

In nuclear power stations artificial radionuclides, mainly fission products and transuranium elements, are produced and the optimal conditions of final storage of the resulting radioactive waste are still a subject of discussion. By detonation of nuclear weapons, by nuclear weapon tests and nuclear accidents, considerable amounts of fission products and radioactive isotopes have been set free and distributed via the atmosphere as radioactive fallout over large areas [2].

1.2 Objective

The aim of this diploma thesis was to attain information on the ^{236}U and $^{239(40)}Pu$ distribution in sea and river water. Therefore, a chemical procedure for the uranium and plutonium separation from large water samples was developed. The method was then tested on tap water, mine water, and artificial sea water. By assessing the $^{236}U/^{238}U$ and $^{240}Pu/^{239}Pu$ isotopic ratios, one is able to attest by which kind of nuclear activity a certain sample had been affected. Sampling of river water and sea water was done in different regions of the world. Accurate coordinates for the sample locations are given in table 1.

table 1: location of samples

sample	water	N [°]	E [°]
La Palma	Atlantic Ocean	28.718	-17.992
Rio Negro	Rio Negro	-3.061	-60.414
Maliuc	Danube	45.175	29.107
Hawaii	Pacific ocean	19.557	-155.966
Irish Sea	Irish Sea	54.4	-3.55
Black Sea	Black Sea	44.430	28.769

1.3 Chemical Procedures

For α-spectroscopy of uranium, ^{232}U spike (0.01445 ± 0.0009 Bq/ 10µL; September 30, 2005) and Fe^{3+}-solution (Fe^{3+} 10mg per 1 L of water sample) was added to the acidified water samples. The addition of NH_4OH-solution leads to a precipitation containing also the actinides, that can be redissolved and uranium is separated using a column filled with UTEVA® resin. After micro-precipitation with NdF_3, ^{238}U, ^{235}U and ^{232}U were detected using α-spectrometry.

For the detection of ^{236}U and the $^{240}Pu/^{239}Pu$ isotopic ratio, AMS (accelerator mass spectrometry) measurement was deployed. The sample preparation consisted of adding a spike mix composed of the isotopes ^{233}U and ^{242}Pu, followed by the same co-precipitation technique as for α-spectrometry. Next, plutonium was separated using 1x8 Dowex® resin and then uranium separation was carried out by application of UTEVA® resin. The targets for AMS were prepared by co-precipitation with iron hydroxide and heating in a furnace.

Filters that had been already measured by α-spectrometry were redissolved using nitric acid and hydrochloric acid and also measured by AMS.

Figure 1 shows a chart of the sample preparation method applied prior to measurement with accelerator mass spectrometry.

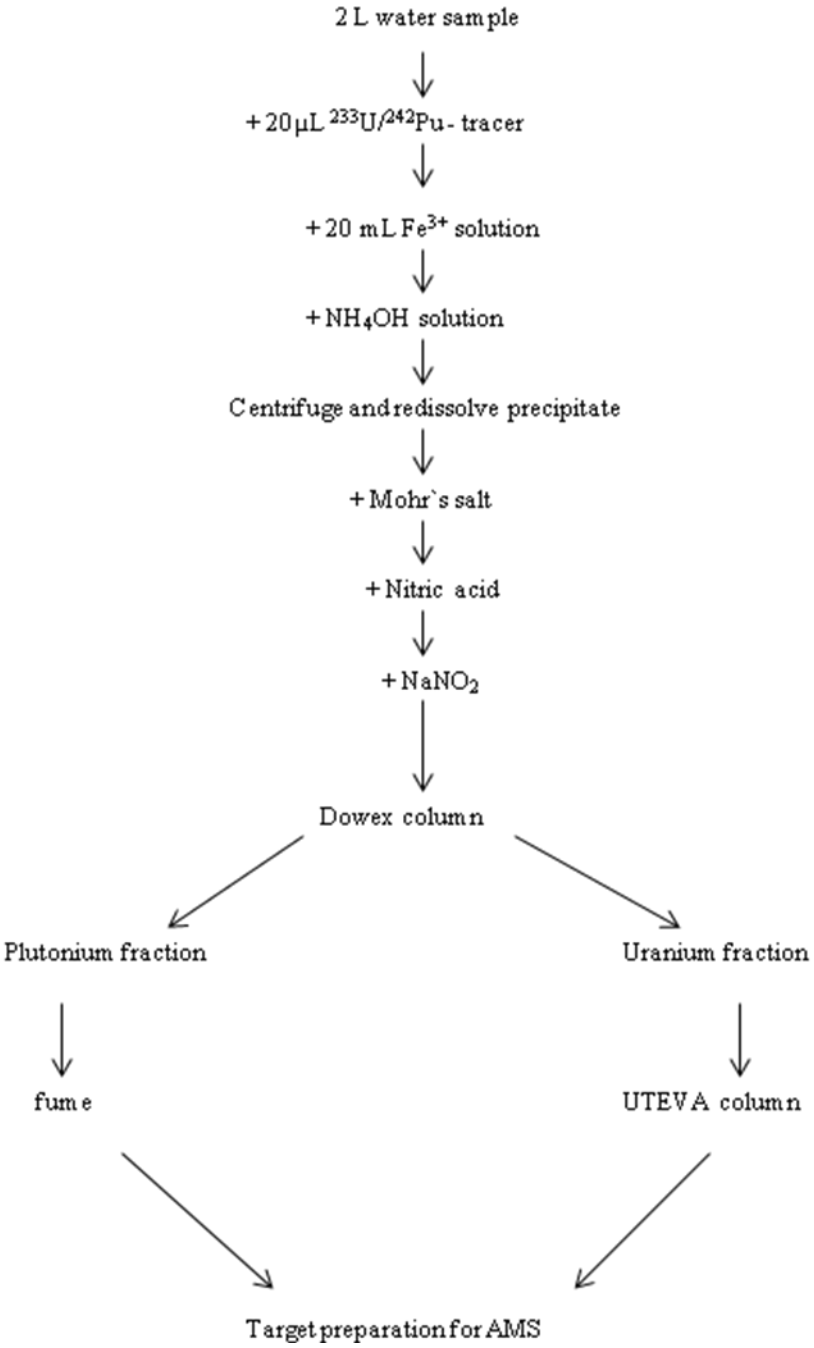

figure 1: chart of sample preparation for AMS

2 The Radionuclides Pu and U

2.1 Preface

While natural thorium and uranium are relatively abundant in the earth`s crust (5 – 20 µg Th and 1 – 10µg U per g), the concentrations of other actinides were originally insignificantly small. However, human activity led to a considerable increase of these nuclides in the last decades. This phenomenon is due to various causes:

· atmospherical nuclear bomb tests in the years between 1950 – 1963, which released 4.2 tons of plutonium and radioactive daughter products into the atmosphere (of which 90% are by now already deposited on the earth)

· surface or underground nuclear bomb tests with a release of 1.4 tons of plutonium

· satellites powered by ^{238}Pu energy sources that burnt up when re-entering the atmosphere

· burnt fuel of nuclear reactors (1 ton of uranium leads, after a period of 3 years in a reactor, to 35 kg fission products and 15 kg plutonium as well as transplutonium elements) [3] .

2.2 Uranium

Uranium, the heaviest naturally occurring element on earth, was discovered in 1789 by Klaproth. Today, it plays an important role in daily life because of its use in nuclear power plants [4].

The content of uranium in the earth`s crust is estimated to amount to 10^{14} – 10^{10} tons, with concentrations of 1 – 10 µg U per g of earth crust and 0.01 – 10 µg per liter of water [3]. Naturally occurring uranium consists mainly of the primordial nuclides ^{238}U and ^{235}U and of ^{234}U, which is part of the uranium-radium decay series [5]. The natural abundances of those uranium isotopes are approximately 99.3% ^{238}U, 0.72% ^{235}U and 0.005% ^{234}U [5]. These ratios may have small variations depending on the geographic origin of the sample, due to natural isotope fractionation, nuclear reactions or anthropogenic contamination [4].

2.2.1 ^{236}U

^{236}U is an α-emitter with a half-life of $2.3 \cdot 10^7$ years. It does occur in nature, but only at ultra-trace concentrations. The $^{236}U/^{238}U$ atom ratios of environmental samples range from 10^{-14} to 10^{-10} and ratios higher than 10^{-9} are regarded to be a clear indicator of anthropogenic contamination [5].

^{236}U can be formed by various ways. First of all by $^{235}U(n,\gamma)^{236}U$ and $^{238}U(n,3n)^{236}U$ reactions. The thermal neutron capture cross section of the $^{235}U(n,\gamma)^{236}U$ reaction is 95 barns, which is about 1/6 of the fission cross section (586 barns) [6]. In nature, this way of forming ^{236}U is enabled by neutrons produced from (α,n)-reactions on lighter nuclei such as Na and Mg and from spontaneous fission of ^{238}U. When thermal neutrons interact with ^{235}U, the probability for fission is about 85%, whereas formation of ^{236}U happens with a probability of 15% [5].

Thermal neutrons derived from cosmic rays can also induce production of ^{236}U on the earth`s surface [7, 8]. Another source of ^{236}U in nature is the growth from ^{240}Pu already deposited on land by global fallout [9]. ^{236}U in global fallout originates mostly from $^{238}U(n,3n)^{236}U$ reactions with fast neutrons and a minor contribution is from $^{235}U(n, \gamma)^{236}U$ reactions [9]. Additionally, a greater amount of ^{236}U is produced in nuclear reactors, also via the thermal neutron capture on ^{235}U [6].

The global inventory of natural ^{236}U is estimated to be about 30 kg ^{236}U in the upper layers of land surface and less than 0.5 kg in the oceans [5].

The anthropogenic inventory of ^{236}U is in the order of 10^6 kg, based on the assumption that the total uranium mined till 2003 adds up to 2.2×10^9 kg and assuming 50% of the ^{235}U were actually used up in reactors [5].

In future, ^{236}U could be a valuable tracer in hydrology and oceanography, be used for exposure dating of very old surfaces and might even become useful in the field of uranium prospecting [5].

2.3 Plutonium

^{239}Pu with a half-life of 24,100 years is formed by irradiation of ^{238}U with neutrons. It occurs in nature only in trace amounts, but is produced in large quantities from nuclear fuel during reactor activity [6].

$$^{238}_{92}U(n,\gamma)^{239}_{92}U \xrightarrow{\beta^-} ^{239}_{93}Np \xrightarrow{\beta^-} ^{239}_{94}Pu$$

The open ocean Pu distribution is due to global fallout, however, there are visible contributions over this background which are mainly due to discharges from reprocessing plants (e. g. Sellafield, La Hague) and close-in fallout from nuclear bomb tests (e. g. the Marshall Islands, Mururoa and Fangataufa Atolls). [10] According to estimations, 12 PBq ($12 \cdot 10^{15}$ Bq) of $^{239+240}$Pu were deposited in the World Ocean from atmospheric nuclear weapons tests [11]. Table 2 gives an overview of the estimated Pu inventory in the world`s oceans originating from those tests. The ^{238}Pu and ^{241}Pu values are decay corrected to January 1st, 2000.

table 2: Estimated Pu isotope inventory in PBq (10^{15}Bq) in the world`s oceans originating from atmospheric nuclear weapons tests [11,12]

	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
Arctic Ocean	0.002	0.05	0.04	0.17	0.00001
Atlantic Ocean	0.05	1.38	0.89	4.24	0.0003
North Atlantic	0.04	1.1	0.7	3.4	0.00023
South Atlantic	0.01	0.3	0.2	0.9	0.00006
Indian Ocean	0.02	0.56	0.36	1.73	0.0002
Pacific Ocean	0.35	4.47	3.98	23.89	0.003
North Pacific	0.17	2.7	2.3	13.5	0.0015
South Pacific	0.07	1.8	1.7	10.4	0.0015
Southern Ocean	0.005	0.07	0.05	0.24	0.00006
All Oceans	0.4	6.5	5.4	30	0.004

Due to the similar reduction potential of Pu^{III}/Pu^{IV} (+ 1.01 V), Pu^{IV}/Pu^{V} (+ 1.04 V) and Pu^{V}/Pu^{VI} (+ 1.02 V), all four oxidation states III, IV, V, VI of plutonium exist alongside in aqueous solution [3]:

$$Pu^{4+} + Pu^{V}O_2^{+} \Leftrightarrow Pu^{3+} + Pu^{VI}O_2^{2+}$$

Compared to uranium, the amount of plutonium found in sea water is significantly smaller with activity concentrations in the range of $0.8 \cdot 10^{-3}$ to $9.2 \cdot 10^{-3}$ mBq/L for the Pacific Ocean, for instance [13]. This is due to the fact that plutonium attaches to a higher extent to particles and settles to the ground, whereas uranium dissolves more readily in water. Therefore, most of the research regarding the distribution of plutonium in the marine environment either focuses on the detection of plutonium in sea sediment and biota or requires the employment of huge water samples. Therefore, much effort has been made recently to improve the sensitivity of the analysis methods for Pu isotopes. As a result, high-capacity analytical procedures such as high resolution inductively coupled plasma mass spectrometry (ICP-MS), thermal ionization mass spectrometry (TIMS) and accelerator mass spectrometry (AMS) were established as methods for the detection of Pu [10].

2.4 Isotopic Composition

As the isotopic composition depends on the source of contamination, the investigation of the isotopic compositions of uranium and plutonium can give valuable information on the origin of the sample.

2.4.1 $^{236}U/^{238}U$

Natural $^{236}U/^{238}U$ ratios in the range of 10^{-14} for environmental samples and 10^{-10} for uranium bearing ores, have been reported in literature, but so far no widespread survey has been completed because levels are too low for routine detection by techniques other than AMS [14,15]. If the $^{236}U/^{238}U$ ratio is higher than 10^{-9}, it can be assessed that the sample has been exposed to a significant neutron flux [15].

^{236}U can figure as a useful tracer of environmental processes and also carry a key signature to differentiate uranium sources [16]. The detection of ^{236}U in environmental samples could be used, for example, to trace effluent uranium in environmental pathways (e.g. ocean transport) or food chains, to detect potential anthropogenic sources in the ocean (e.g. from sunken submarines) or even as a means to identify uranium used in depleted uranium weapons, or illicit nuclear activities [17].

2.4.2 $^{240}Pu/^{239}Pu$

As plutonium is mainly produced from neutron irradiation of uranium, the isotopic composition of plutonium is a function of the neutron intensity and the duration of irradiation and thus a characteristic fingerprint of the source. The $^{240}Pu/^{239}Pu$ and $^{238}Pu/^{239+240}Pu$ ratios vary depending on the production process and therefore their measurement allows the reconstruction of the history of the neutron exposure to a sample. Longer irradiation and higher fluxes lead in general to a higher content of the heavier isotopes [18].

The $^{240}Pu/^{239}Pu$ atomic ratio is typically low (0.02-0.06) in weapon-grade Pu. Plutonium used in nuclear reactors, on the other hand, is characterized by a content of 35% ^{239}Pu and manifests a much higher $^{240}Pu/^{239}Pu$ atomic ratio of 0.2-1.0 after fuel burn-up [19]. The mean $^{240}Pu/^{239}Pu$ atom ratio and $^{238}Pu/^{239+240}Pu$ activity ratio for global fallout from atmospheric weapons testing in the years from 1945 to 1980 were found to be 0.178 ± 0.023 and 0.019 ± 0.006 respectively [20]. For the Chernobyl accident, the ratio is one order of magnitude higher, values for the $^{240}Pu/^{239}Pu$ ratio are 0.38 ± 0.07 and for $^{238}Pu/^{239+240}Pu$ 0.42 ± 0.04 [19]. Some characteristic data for the atom ratio of $^{240}Pu/^{239}Pu$ and the activity ratio of $^{238}Pu/^{239+240}Pu$ is depicted in table 3. The $^{238}Pu/^{239+240}Pu$ activity ratio is decay corrected to the year 2000.

table 3: plutonium isotopic ratios [19]

Source	^{240}Pu / ^{239}Pu	^{238}Pu / $^{239+240}Pu$
	atom raio	activity ratio
global fallout	0.178 ± 0.023	0.019 ± 0.006
test sites		
French Polynesia	0.02 - 0.05	0.1 - 0.4
Semipalatinsk	0.038 ± 0.016	0.037 ± 0.002
releases from the nuclear industry		
Sellafield (up to 1996)	0.06 - 0.25	0.03 - 0.4
La Hague effluent, 1996	0.34 ± 0.06	
Accidental releases		
Chernobyl accident, 1986	0.38 ± 0.07	0.42 ± 0.04
Thule accident, 1968	0.055 ± 0.008	0.0161 ± 0.0010
Palomares accident, 1966	0.063 ± 0.006	0.015 ± 0.004

3 Experimental Procedures

3.1 General Procedures

a. Cleaning

Both for α-spectrometry and AMS sample preparations, all labware was thoroughly cleaned by boiling with concentrated hydrochloric acid for one hour followed by rinsing with distilled water and 3 times using millipore® water.
Plastic equipment, for instance 50 mL vials, were rinsed with 10 % nitric acid solution and afterwards washed with distilled water and 3 times using millipore® water.

b. Storage of samples

Great care was taken during the work to prevent degradation of samples. Preparation procedures took several days and sample solutions were stored over night exclusively in acidified forms and protected from dust.

c. Uranium micro-precipitation with NdF_3

For the micro-precipitation, 50 µL of 1 mg / mL Nd^{3+} solution, 6 – 8 drops of 15 % $TiCl_3$ solution and 5 mL 40 % hydrofluoric acid were added. The solution was allowed to stand for half an hour, then shaken and allowed to stand for another 30 min. A cellulose nitrate membrane filter was used for the micro-precipitation. After the sample solution had slowly passed the filter, the vial was washed using 3 x 2 mL 4 % HF and 2 x 2 mL millipore® water. After application of vacuum for 20 minutes, the filter was mounted on a filter holder for measurement by alpha spectrometry. This procedure is based on proceedings described in [21] and [22].

d. Plutonium micro-precipitation with NdF_3

Micro-precipitation for plutonium was done according to methods described in [23].

After fuming, the residue was dissolved using 4 times 5 mL 1 M HNO_3 and 0.5 g Mohr`s salt were added. 0.5 mL of 25 % $NaNO_2$, 50 µL Nd^{3+} (1mg/mL) solution and 5 mL 40 % hydrofluoric acid were added one after another and the solution shaken after each new addition. The solution was allowed to stand for half an hour, then shaken and allowed to stand for another 30 min. A cellulose nitrate membrane filter was used for the micro-precipitation. After the sample solution had slowly passed the filter, the vial was washed using 3 x 2 mL 4 % HF solution and 2 x 2 mL millipore® water. After applying vacuum for 20 minutes, the filter was mounted on a filter holder for alpha spectrometry.

3.2 Preliminary Tests for uranium

3.2.1 Introduction

Three different methods for the analysis of uranium in water samples were tested. The test samples were: Viennese tap water, water from Jachimov (CZ) and self-prepared artificial sea water of the following composition:

table 4: composition of artificial sea water [29]

Substance	M [g/mol]	c [mol/L]	m [g]
Na_2CO_3	105.99	0.0046	0.488
$NaHCO_3$	84.01	0.0184	1.55
NaBr	102.89	0.0008	0.082
KCl	74.55	0.0099	0.738
H_3BO_3	61.33	0.0004	0.025
$CaCl_2$	102.98	0.0103	1.061
$MgCl_2 \cdot 6H_2O$	203.33	0.0532	10.82
Na_2SO_4	142.05	0.0282	4.01
NaCl	58.44	0.409	23.9

For the preparation of artificial sea water, the salts were weighted according to the calculated values shown in table 4. Then, the salts were dissolved in 1 L millipore® water. The pH was checked and if necessary adjusted with 1 M HCl to pH = 8.2, because sea water should show a pH of 8.2.

In order to simulate the natural uranium concentration in sea water, which is 3µg of ^{238}U per L [24], 2.1 µL of ^{238}U solution (^{238}U in 7 M HNO_3; 17.6 Bq/mL) were added.

Water originating from the mine in Jachimov, Czech Republic, was expected to show high uranium content, because in this region pitchblende, an ore with high uranium concentrations, is mined.

Tap water was taken directly from the tap in our laboratory and is supposed to show low uranium concentration.

For all three procedures tested, blanks were also analyzed to adjust the final sample results. For these blanks, 1 L of millipore® water was subjected to the same proceedings as the samples.

table 5: list of water samples for preliminary tests

sample	water	method number
TW1	tap water	1
kMeer1	artificial sea water	1
Jach1	water from Jachimov	1
blank1	millipore water	1
TW2	tap water	2
kMeer2	artificial sea water	2
Jach2	water from Jachimov	2
blank2	millipore water	2
TW3	tap water	3
kMeer3A	artificial sea water	3
kMeer3B	artificial sea water	3
Jach3	water from Jachimov	3
blank3	millipore water	3

For preliminary tests, 10 µL of ^{232}U spike solution (0.01445 ± 0.0009 Bq / 10 µL; September 30, 2005) were added to 1 L of the tap water and artificial sea water samples. In the testing of water from Jachimov, 20 µL of this tracer were added, because higher uranium concentrations were expected. Measurement times could therefore be reduced for those samples. After addition of ^{232}U, procedures differ from each other and are described in the following section.

Testing of ^{232}U spike

A micro-precipitation of 20 µL of the ^{232}U spike (0.0289 ± 0.0018 Bq / 20 µL; September 30, 2005) in 20 mL 1 M HCl was done in order to check whether the micro-precipitation represents a step that reduces the chemical yield significantly. The sample was then measured by both α-spectrometry (measurement time: 252,000 s) and AMS.

3.2.2 First U-separation method: Preconcentration of water samples by evaporation and use of Dowex® 1x2 resin

The water samples were evaporated to dryness. The residue was dissolved in 3 x 10 mL HCl and evaporated to dryness after each addition of hydrochloric acid. After the last evaporation, the residue was dissolved in 8 M HCl. A column was filled with Dowex® 1x2 resin (100-200 mesh) in millipore water. After conditioning the column with 4 x 10 mL 8 M HCl, the sample solution was loaded. Next, the column was washed with 2 x 25 mL 8 M hydrochloric acid in order to remove Th^{4+} and Ca^{2+}. Then uranium was eluted using 2 x 40 mL 0.1 M HCl and this solution was evaporated to dryness.

The residue was fumed 3 times using 5 mL concentrated HNO_3 and 0.5 mL 30% H_2O_2 solution and evaporated to dryness. Next, the residue was redissolved and fumed using 3 times 5 mL HCl. Eventually, the residue was transferred with 4 x 5 mL 1 M hydrochloric acid to a 50 mL vial for micro-precipitation (see 3.1.c).

3.2.3 Second U-separation method: Co-precipitation with $Ca_3(PO_4)_2$ and use of UTEVA® resin

This method was done using chemical procedures described by Eichrom Technologies Inc. (see [25]).

After addition of 0.5 mL 1.25 M $Ca(NO_3)_2$ to one liter of the acidified water samples, the beakers were covered with a watch glass and heated until boiling. Then, 200 µL of 3.2 M

$(NH_4)_2HPO_4$ solution were added and the pH was adjusted to pH=8-10 using concentrated NH_4OH solution, which resulted in the forming of a white, cloudy precipitate. The samples were heated for another 30 minutes and allowed to cool down. The supernatant was decanted and the solution centrifuged (4,000 rpm, 8 min). The collected precipitate was washed 2 times with millipore® water.

The precipitate was dissolved in 5 mL nitric acid, evaporated to dryness and redissolved in 10 mL 3 M HNO_3.
A column filled with UTEVA® resin was conditioned using 3 x 5mL 3 M HNO_3. After bringing the sample solution on the column, the beaker was rinsed with 2 x 10 mL 3 M HNO_3. Then, the column was washed with 5 mL 9 M HCl and 20 mL 5 M HCl. Uranium was eluted using 30 mL 0.01 M HCl.
The sample solution was evaporated to dryness and fumed with 3 times 5 mL concentrated HNO_3 and 0.5 mL 30% H_2O_2 and then evaporated and redissolved in 3 x 5 mL HCl. The residue was dissolved in 4 x 5mL 1 M HCl prior to micro-precipitation.

3.2.4 Third U-separation method: Co-precipitation with $Fe(OH)_3$ and use of UTEVA® resin

The water samples were acidified to pH = 2 using 10 % HNO_3 solution. 10 mL Fe^{3+}-solution (10 mg of Fe^{3+} per 1 L of water sample) were added and the samples were heated for 2 hours at 70 – 80 °C and stirred using a magnetic stirrer or a glass rod. Next, NH_4OH solution was added to adjust pH = 8 – 9. This resulted in the forming of a red precipitate, which was allowed to mature over night.

The next day, the supernatant was decanted and the solution centrifuged (4,000 rpm / 12 min). The precipitate was dissolved in 5 mL nitric acid, evaporated to dryness and redissolved in 10 mL 3 M HNO_3.
A UTEVA-column was conditioned with 3 x 5mL 3 M HNO_3. After the sample solution was brought on the column, the beaker was rinsed with 2 x 10 mL 3 M HNO_3. Then, the column was washed with 5 mL 9 M HCl and 20 mL 5 M HCl. Uranium was eluted using 30 mL 0.01 M HCl.

The sample solution was evaporated to dryness and redissolved 3 times in 5 mL HNO_3 and 0.5 mL 30% H_2O_2 solution and then fumed using 3 times 5 mL concentrated hydrochloric acid. The residue was dissolved in 20 mL 1 M HCl for micro-precipitation.

After micro-precipitation with NdF_3, the samples were measured by α-spectrometry.

3.2.5 Choosing a method after preliminary tests (U-separation)

The first method was deemed not suitable for large sea water samples, because the salts of the artificial sea water sample precipitated too early during the evaporation step. They could not even be redissolved in large amounts of acid (335 mL of 8 M HNO_3) and had to be discharged before loading the sample onto the column.
Method 2 was better suitable for sea water samples, but best results for chemical yields were obtained using the third method. Furthermore, the third method also proofed to be advantageous for the handling of large water samples. However, first test experiments also showed lower ^{238}U yield than samples subjected to procedures number 1 and 2. This yield was improved by heating the samples for longer times (6-8 hours).

3.3 Preliminary tests for combined U and Pu detection

3.3.1 Introduction

Two different methods were tested for the combined detection of uranium and plutonium. In both cases, the co-precipitation with $Fe(OH)_3$ represented the first step, as it had proved to be most useful in the preliminary tests for uranium. Tap water was analyzed using both procedures, artificial sea water was also analyzed using the first method.

Samples and detectable isotopes are listed in table 6.

table 6: list of samples for combined U and Pu tests

sample	water	isotopes	method number
TW_01_Pu	tap water	^{242}Pu	1
TW_01_U		^{232}U, ^{234}U, ^{238}U	1
kMeer_01_Pu	artificial sea water	^{242}Pu	1
kMeer_01_U		^{232}U, ^{234}U, ^{238}U	1
TW_02_Pu	tap water	^{242}Pu	2
TW_02_U		^{232}U, ^{234}U, ^{238}U	2

3.3.2 Testing of ^{242}Pu spike

3.3.2.1 Introduction

Both liquid scintillation counting and alpha spectrometry were applied to verify the activity concentration of the ^{242}Pu spike solution. This spike solution had been measured and labeled in 1996. Therefore, checking the accuracy of the activity concentration was deemed to be necessary. As this tracer is frequently used, some of the solution may have evaporated during this long period of time, leading to a change in concentration.

3.3.2.2 Testing of ^{242}Pu spike solution by LSC

First of all, liquid scintillation counting was used for the verification of the ^{242}Pu spike.
For the LSC measurement, 100 µL of the spike solution and 20 mL of scintillation cocktail were filled in an LSC vial and measured for 120 s. 100 µL of 3 M HNO_3 together with 20 mL scintillation cocktail were used as a blank.

3.3.2.3 Testing of ^{242}Pu spike solution by α-spectrometry after direct evaporation

Three identical tests were done to check the activity concentration of the ^{242}Pu tracer with α-spectrometry. For this purpose, small metal plates were rinsed in 7 M HNO_3 and put on a heater. 20 µL of spike solution were dropped onto the plates and evaporated to dryness. Then the metal plates were measured by α-spectrometry for 150,000 s.

3.3.2.4 Testing of ^{242}Pu spike solution after micro-precipitation step

Two micro-precipitations of 20 µL of the ^{242}Pu spike in 20 mL 1 M HNO_3 solution were done. For the first test, the membrane filter was positioned face-up in regard to the orientation in the package and for the second test, it was placed the other way round. The aim was to check whether the positioning of the filter during the micro-precipitation had any effect on the analytical results.

3.3.3 First method for combined U and Pu determination: using 1x2 Dowex® and UTEVA® resin

After adjusting an amount of one liter of the samples (tap water TW_01 and artificial sea water kMeer_01) to pH = 2, 10 µL of ^{232}U spike solution (0.01445 ± 0.0009 Bq / 10µL; September 30, 2005), 20 µL ^{242}Pu tracer (A = 0.0958 ± 0.0049 Bq / 20 µL; October 11, 2010) and 10 mL Fe^{3+} solution were added. The samples were heated for 7 hours and stirred at times. Then, NH_4OH solution was added to adjust pH = 8 – 9 and the resulting precipitate was allowed to mature over night.

After centrifugation, the precipitate was dissolved in 20 mL 8 M HNO_3, 0.2 g of $NaNO_2$ were added and the solution was heated gently till the formation of nitrous gases stopped. A Dowex® 1x2 100-200 mesh column was prepared by conditioning with 4 x 10 mL 8 M HNO_3 and the sample solution was loaded onto the column. 3 x 15 mL 8 M HNO_3 were brought on the column and these first two fractions were used for the analysis of uranium.

Next, 3 x 10 mL concentrated hydrochloric acid was used to remove Fe, Ca, Am and Th. Finally, plutonium was eluted using 50 mL of a solution consisting of 0.36 M HCl / 0.018 M HF and collected in a teflon beaker, filled beforehand with 5 mL concentrated nitric acid. This solution was gently evaporated to dryness and fumed 3 times with 5 mL concentrated HNO_3 and 0.5 ml 30 % H_2O_2 solution. After dissolving the residue in 20 mL 1 M HNO_3, Pu was precipitated (see 3.1.c) and measured by alpha spectrometry.

The uranium fraction was treated according to 3.2.4 (Third U-separation method) and also measured using alpha spectrometry.

3.3.4 Second method for combined U and Pu determination: using 1x8 Dowex® and UTEVA® resin

The precipitation step was done in the same way as for the first method (3.3.3).
The next day, the sample was centrifuged and the residue dissolved in 20 mL 1 M HNO_3. 100 mg Mohr`s salt $(NH_4)_2Fe(SO_4)_2 \cdot 6\ H_2O$, 20 mL concentrated HNO_3 and 0.5 g $NaNO_2$ were added and the solution heated gently till the point at which no nitrous gases formed any more.

For the separation of plutonium, a column filled with Dowex 1x8 resin was conditioned using 4 times 10 mL 8 M HNO_3. The sample solution was loaded onto the column, the beaker rinsed using 4 times 10 mL 8 M HNO_3 and this solution was also passed through the column. These two fractions were combined for uranium analysis.

Next, 50 mL concentrated HCl were used to remove Fe, Am, Th and Ca from the column. Plutonium was eluted using 50 mL of a 0.1 M NH_4I – 9 M HCl solution. The plutonium fraction was evaporated to dryness and fumed using 3 times 5 mL HNO_3 and 0.5 mL 30 % H_2O_2 solution. The residue was dissolved in 20 mL 1 M HNO_3 and measured by alpha spectrometry after micro-precipitation (see 3.1.d).

For further treatment of the uranium fraction, a column filled with UTEVA® resin was conditioned using 3 times 5 mL 3 M HNO_3. After the sample solution was brought on the column, the beaker was rinsed with 2 x 10 mL 3 M HNO_3. Then, the column was washed with 5 mL 9 M HCl and 20 mL 5 M HCl. Uranium was eluted using 30 mL 0.01 M HCl.
The sample solution was evaporated to dryness and redissolved 3 times in 5 mL HNO_3 and 0.5 mL 30% H_2O_2 solution and then fumed using 3 times 5 mL concentrated hydrochloric acid. The residue was dissolved in 20 mL 1 M HCl for micro-precipitation (see 3.1.c).

3.3.5 Choosing a method for combined U and Pu detection

For application on the real samples, the second method was chosen, as it proved to be less time consuming and therefore less prone to contamination. In the first method, the cleaning step using concentrated HCl took several hours (approximately 5-6). Furthermore, the use of

teflon beakers asks for a more gentle and slow evaporation during which the risk of contamination from dust and particles in the air is greater.

The spectra obtained from the second method showed better energy resolution. In the case of the first method, a ^{242}Pu peak could be observed in the uranium spectra of tap water (TW_01_U), suggesting that the method did not completely separate uranium from plutonium.

3.4 Sea and river water samples

3.4.1 Location of samples

Samples were collected far from known contaminated sites, with the exception of water from the Irish Sea, which is known to be affected by the Sellafield reprocessing plant. Since 1952, low-level liquid radioactive waste was permitted to be discharged from the Sellafield plant to the marine environment. Discharge rates reached a maximum in the 1970s but have been reduced by approximately two orders of magnitude since then. However, discharge of $^{239(40)}$Pu from Sellafield was 5.92 TBq (10^{12} Bq) up to the end of 1992, which makes up to 45% of the estimated inventory of $^{239(40)}$Pu in the North Atlantic ocean [26].

table 7: location of water samples

sample	water	N [°]	E [°]
La Palma	Atlantic Ocean	28.718	-17.992
Rio Negro	Rio Negro	-3.061	-60.414
Maliuc	Danube	45.175	29.107
Hawaii	Pacific ocean	19.557	-155.966
Irish Sea	Irish Sea	54.4	-3.55
Black Sea	Black Sea	44.430	28.769

3.4.2 Sample preparation

The samples were analyzed both by α-spectrometry for determination of ^{238}U and ^{234}U content and by AMS technique to explore the ^{236}U/^{238}U and ^{240}Pu/^{239}Pu isotopic ratios. The water samples were collected in clean plastic bottles. In the laboratory, the samples were first acidified, then shaken thoroughly and left for some days in order to prevent uranium and

plutonium from settling to the walls of the bottles and also to bring already settled isotopes back in solution.
Samples bearing visible suspended particles or even sediment were filtered through a Whatman^{TM} 44 filter prior to analysis.

The water samples were split for the application of the two different sample preparation methods for α-spectrometry (1 L) and AMS (2 L deployed) measurement.

3.4.3 Chemical Procedures for uranium measurement by α-spectrometry

Alpha spectrometry was used for the measurement of ^{234}U and ^{238}U content. However, it could not be applied for the Pu measurement, because of the low levels of this isotope in water samples.

Table 8 contains a list of the sample volumes used in the preparation method for alpha spectrometry.

table 8: volume of water samples for α-spectrometry

sample	water	volume [mL]
La Palma	Atlantic Ocean	986.5
Rio Negro	Rio Negro	1,010
Maliuc	Danube	1,078
Hawaii	Pacific ocean	1,471
Irish Sea	Irish Sea	1,000
Black Sea	Black Sea	1,454
blank	millipore water	1,000

For the determination of the ^{238}U and ^{234}U content by α-spectrometry, 20 µL of ^{232}U spike solution (0.0289 ± 0.0018 Bq / 20 µL; September 30, 2005) were added to the water samples. The co-precipitation with $Fe(OH)_3$ (see 3.2.4; Third U-separation method) and micro-precipitation with NdF_3 (see 3.1.c) were applied. The amount of added Fe^{3+} solution was calculated individually for each sample, because sample volumes varied, as it is shown in table 8.

3.4.4 Chemical Procedures for U and Pu measurement by AMS

3.4.4.1 Introduction

Special strategies were adopted in order to ensure the purity of the employed chemicals and therefore prevent contamination by laboratory equipment. This approach is necessary, because ^{236}U and plutonium concentrations in sea water are extremely low and even minor contamination may strongly influence results.

3.4.4.2 Materials, Acids and bases

Nitric Acid was distilled for purification using an acid destillation unit made of quartz glass, which is shown in figure 2.

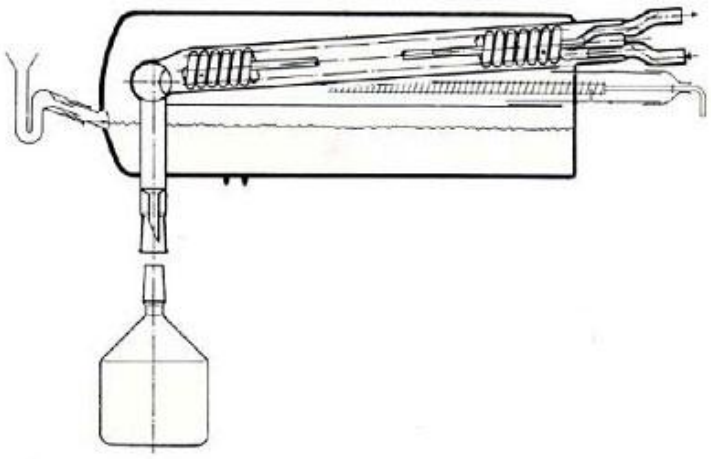

figure 2: Acidest distillation unit [27]

Surface evaporation is the principle of this distillation unit. Unlike in the case of boiling evaporation, no vapor or aerosol is produced and the obtained distillate is of very high purity. In this distillation unit, contact of liquid and sockets is avoided. The sockets of filling tube and collecting tube are arranged in a way that drains impurities to the outer wall. Acid is introduced into the apparatus through a specially formed funnel. This funnel is then rotated by 90° in operating state and so the U – shaped outlet is filled with acid and acts like a syphon between apparatus and outer atmosphere [27].

Nitric Acid was always prepared freshly in order to avoid any contamination from storage. A voltage regulator was used to adjust power supply for the distillation unit to 100 V. It took about 8 hours to purify 250 mL of nitric acid.

Hydrochloric Acid was passed through a column filled with UTEVA® resin. In this case, 9 M HCl was loaded onto the column because literature suggests that UTEVA® resin is most performant at this molarity [28]. Required hydrochloric acid of lower molarity was then prepared from the purified 9 M HCl. Concentrated hydrochloric acid was also purified using UTEVA® resin, but not used for dilutions.
By applying this strategy for purification of hydrochloric acid, about 200 mL of HCl were purified in a time period of 6 hours.

Millipore® water was used for the preparation of dilutions and cleaning of all laboratory equipment.

Furthermore, Suprapur® ammonia solution, Suprapur® hydrogen peroxide and mono-element iron standard were used.

3.4.4.3 Spike for AMS

The concentration of the mixed $^{233}U/^{242}Pu$ spike used for AMS sample preparation was $4.76 \pm 0.05 \cdot 10^{10}$ atoms ^{233}U per g and $2.69 \pm 0.03 \cdot 10^{11}$ atoms ^{242}Pu per g. It was stored in 5 M nitric acid. 20 µL of this spike were added to each water sample and the bottle was weighted before and after use to conduct a correction due to evaporation if necessary. The spike is traceable to IRMM-058, sample identification 0008 for ^{233}U and 0087 for ^{242}Pu.

3.4.4.4 Water samples for AMS

20 µL of a $^{233}U/^{242}Pu$ spike solution were added to 2 L of the acidified (pH = 2) water samples and $Fe(OH)_3$ precipitation was done according to 3.3.3.

The second method of the preliminary tests for combination of Pu and U (see 3.3.4) was used for the separation of plutonium and uranium.

In order to obtain samples suited for measurement with AMS, a target preparation had to be done.

3.4.4.5 Target preparation

After evaporation, the sample residue was taken up in 2 mL concentrated hydrochloric acid. After addition of 7 mL H_2O and 1 mL Fe^{3+} solution (1 mg Fe^{3+} / mL), 25 % NH_3 solution was added drop by drop till the forming of a red precipitate. After the pH had been reduced to pH=8 – 9 by heating on a water bath, the precipitate was centrifuged for 15 minutes at 4,000 rpm. The supernatant was decanted and the precipitate dried at 100°C for 2 hours in an electric oven. The samples were transferred to small Quartz cups for calcination at 800°C for 2 hours in a muffle furnace. The resulting oxides were pressed into small sample holders made of aluminium, which are convenient for the use in the ion source of the AMS facility.

Figure 3 shows a graph of the temperature program deployed in the target preparation for AMS measurement.

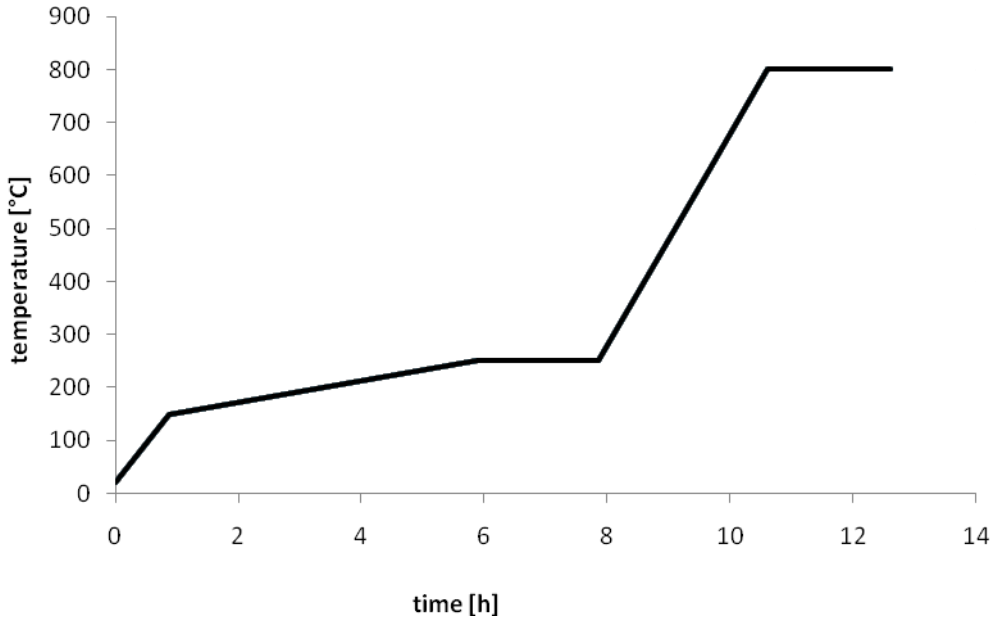

figure 3: temperature program muffle furnace

3.4.4.6 Blanks for AMS

In order to determine the amount of inherent contamination of the applied sample preparation, 2 L of bidistilled water and 2 L of millipore® water were treated in the same way as the water samples and measured by AMS. Results showed that the input of actinides from millipore water was lower and thus millipore® water was used for all dilutions of acids and washing of laboratory apparatus.

Whether or not the ammonia solution contributes to the measured amount of actinides was investigated by evaporating 80 ml of Suprapur® ammonia solution to dryness, followed by the target preparation for AMS.

3.4.4.7 In-house standard Vienna – KkU

A large amount of uranyl nitrate that was mined before 1918 in Joachimsthal (Czech Republic) is stored at the former Radiuminstitut in Vienna. Therefore, this ore represents the natural isotopic ratio of uranium isotopes for pre-nuclear times. This in-house standard was calibrated to $^{236}U/^{238}U = (6.98 \pm 0.32) \cdot 10^{-11}$ using a certified reference material (IRMM REIMEP – 18 A) [5].

3.4.4.8 Redissolving filters for AMS

The samples of the preliminary tests after α-spectrometry were also analyzed by AMS. Therefore, the filters were redissolved using 3 times 5 mL HNO_3 and 1 mL 30 % H_2O_2 solution, evaporated to dryness after each addition and then the solutions were fumed 3 times with 5 mL HCl. Afterwards, the target preparation (see 3.4.4.5) for AMS measurement was applied.

4 Measurement Techniques

4.1 Introduction

^{238}U and ^{234}U activity concentrations were measured by alpha spectrometry, whereas AMS was applied for the measurement of ^{236}U / ^{238}U and ^{240}Pu / ^{239}Pu atomic ratios.

4.2 Alpha spectrometry

By using micro-precipitation, thin layers containing the investigated radio-nuclides co-precipitated with NdF_3 can be produced on a membrane filter. The small range of α-particles renders the fabrication of thin layers requisite to avoid self-absorption. Silicon surface-barrier detectors are most suitable for alpha spectrometry. They are operated at room temperature in a vacuum chamber to avoid energy losses. The α-particles are stopped within a thin charge depleted region of the detector and the number of electron-hole pairs is directly proportional to the energy of the α-particles. The charge pulses are integrated in a charge-sensitive amplifier. α-Emitters of known energy are used for the calibration [2].

In this work, alpha spectrometry was conducted using a PIPS (Passivated Implanted Planar Silicon) detector, model 7401 VR, Canberra/Packard with an active area of 450 mm^2. The counting time was 300,000 s and the software Genie 2.1 (Canberra, USA) was used for the evaluation of the spectra.

4.3 AMS – Accelerator mass spectrometry

AMS was developed in order to overcome fundamental limitations of both decay counting and conventional mass spectrometry. In contrast to these methods, accelerator mass spectrometry is well suited for the detection of long-lived isotopes [29]. The particular advantages of AMS are its outstanding abundance sensitivity and the complete suppression of

molecular ion species. Compared to conventional mass spectrometric methods, the detection limit for heavy, long-lived radioisotopes can be improved by several orders of magnitude when AMS is deployed [30].

Mass spectrometry enables one to measure minute isotopic ratios of long-lived nuclides by detecting the atoms directly rather than their infrequent decay as it is done in the case of decay counting. For actinides with half lives longer than 10^3 years, AMS can provide higher detection efficiency than α-spectrometry. Owing to the exceptional sensitivity, the applicability of AMS extends to almost every compartment of the environment in which radionuclides of anthropogenic and/or natural origin occur at detectable levels [30].

Currently two AMS laboratories investigate natural isotopic abundances of $^{236}U/U$ below 10^{-10}: the tandem facility at ANU in Canberra, Australia, and VERA (Vienna Environmental Research Accelerator), Vienna, Austria with lowest $^{236}U/U$ ratio reported on real samples of $1 \cdot 10^{-12}$ and $5 \cdot 10^{-12}$ respectively. Both laboratories have a high-resolution injector magnet and high-resolution magnetic and electric components in the analyzer, followed by a TOF and energy detector [30]. Figure 4 shows the layout of VERA.

In this work, AMS was required for the detection of ^{236}U, because of the low amount of this uranium isotope in environmental samples. The isotopic ratio $^{240}Pu/^{239}Pu$ is also measured by AMS, both because of the scarcity of these isotopes in water samples and their similar alpha energies, which cannot be resolved by alpha spectrometry. For plutonium isotopes, the great advantage of AMS is the complete destruction of molecular isobars (e.g. ^{238}UH for ^{239}Pu), which can cause interference when applying conventional mass spectrometric methods such as TIMS and ICP-MS [31].

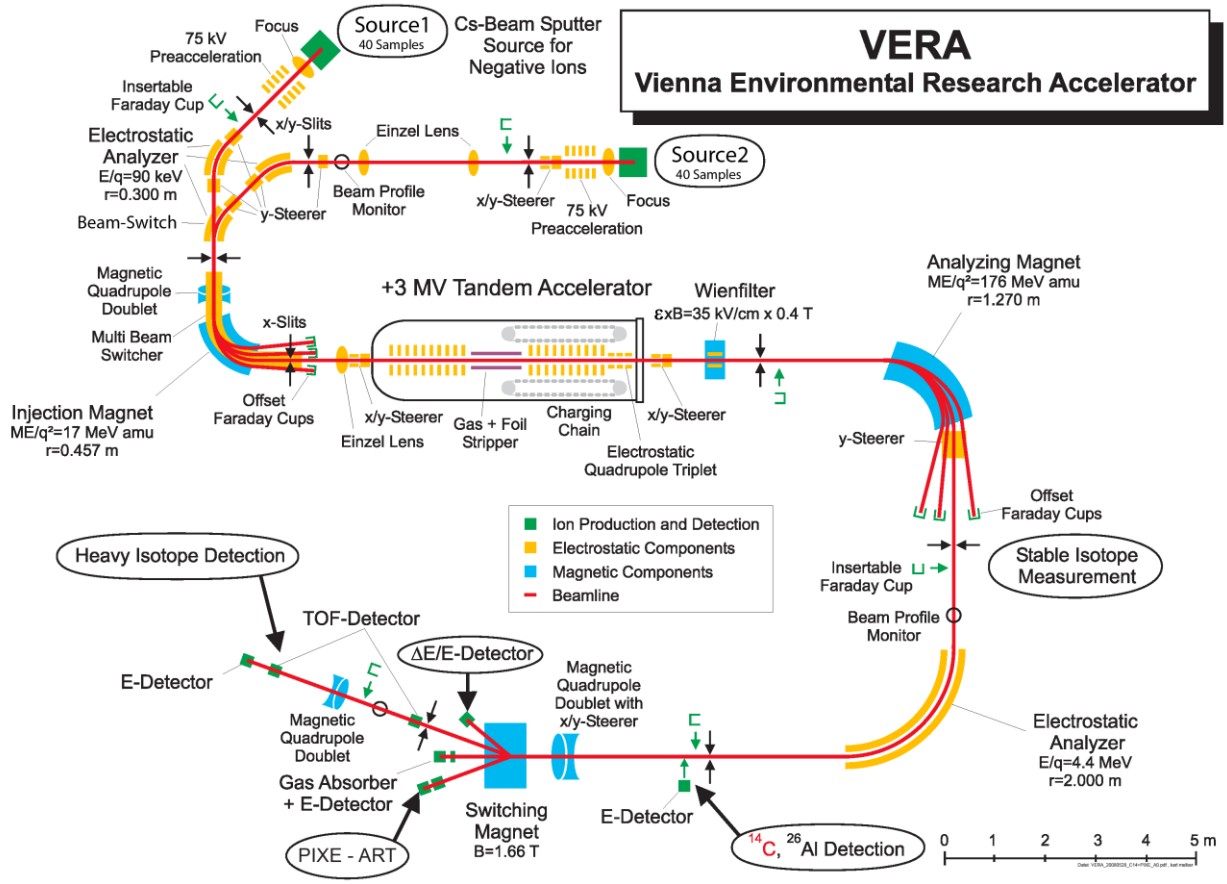

figure 4: VERA AMS facility [32]

5 Results and Discussion

In the following part, results from alpha spectrometry and AMS measurements of both preliminary tests and real samples are outlined and discussed.
The calculated uncertainties represent the 1σ error of the ascertained values.

5.1 Results from Alpha spectrometry

Alpha spectrometry was performed to obtain the activity concentrations of ^{238}U and ^{234}U. Further, this technique was applied for all preliminary tests to check the suitability of the different sample preparation methods for both uranium and plutonium and it was also used to tests the spike solutions. In measurements with alpha spectrometry, the uranium isotopes ^{234}U, ^{238}U and the spike ^{232}U were detected, but in the case of plutonium, only the spike ^{242}Pu could be detected because the detection limit of α-spectrometry does not allow assessment of the low amounts of $^{239/240}Pu$ in water samples. In addition, ^{239}Pu and ^{240}Pu have similar alpha energies and these isotopes cannot be resolved by alpha spectrometry.

For uranium detection, the measurement times varied between 252,000 s and 504,000 s for the preliminary tests, but were adjusted to 300,000 s for all real samples. Accurate measurement times are listed in the attachment.

For plutonium, measurement times were much shorter (around 74,000 s), but these short time periods were sufficient because of the higher activity concentration of the plutonium spike (0.0958 ± 0.0049 Bq / 20 µL; October 11, 2010) compared to the uranium tracer solution (0.0289 ± 0.0018 Bq / 20 µL; September 30, 2005).

5.1.1 Testing of ^{232}U and ^{242}Pu spikes

5.1.1.1 ^{232}U spike solution

Testing of the ^{232}U spike showed that a slight, but measureable diminution of the chemical yield was caused by the micro-precipitation. 20 µL spike solution was used in the process and

the obtained activity concentration was 0.02304 Bq. Taken into account that the real activity concentration is 0.0289 Bq ± 0.0018 Bq / 20 µL (September 30, 2005), the chemical yield of the micro-precipitation step was 83.7%.

table 9: results for testing of ^{232}U spike

sample	A [Bq] / 20µL	± 1σ	yield	± 1σ
^{232}U_01	0.02304	0.00397	0.837	0.153

5.1.1.2 ^{242}Pu spike solution

First, the ^{242}Pu tracer was tested with LSC, because it was expected that the activity concentration might have changed since the last measuring and labeling of the spike solution, which was done in 1996. The original label dating from July 3, 1996 displayed an activity concentration of (0.0631 ± 0.0016) Bq / 20 µL. Liquid scintillation counting provided a much higher activity concentration of 0.479 Bq ± 0.0249 Bq for 100 µL, which corresponds to 0.0985 Bq ± 0.0049 Bq for 20 µL (October 11, 2010 reference date). This increase is probably due to evaporation of the nitric acid, in which the tracer is dissolved.

For all experimental evaluations, the new value of the activity concentration for the ^{242}Pu spike solution, found by liquid scintillation counting, was adopted.

Table 10 displays activity concentrations measured with LSC.

table 10: results testing of spike with LSC (October 11, 2010)

sample	volume [µL]	A [Bq]	± 1σ
^{242}Pu_LSC	100	0.479	0.0249
^{242}Pu_LSC	20	0.0958	0.0049

Measurements of small amounts of the ^{242}Pu spike after evaporation are expected to show the actual activity due to the fact that the solution was evaporated directly without any other prior

preparation steps. Data obtained by liquid scintillation counting corresponds well with results of the testing after evaporation.

table 11: results testing of tracer after evaporation

sample	A [Bq/ 20µL]	± 1σ	yield	± 1σ
^{242}Pu_03	0.09571	0.01642	0.999	0.243
^{242}Pu_04	0.09629	0.01533	1.005	0.236
^{242}Pu_05	0.09559	0.01032	0.998	0.204

Investigation of the micro-precipitation step made clear that some loss had to be expected during this step (see also 5.1.1.1). Generally, no significant difference was observed concerning the orientation of the filters. For ^{242}Pu_02, the membrane filter was oriented like in the package and in the case of ^{242}Pu_01, it was turned around and placed on the filter holder. Results were 0.06968 Bq / 20 µL and 0.07226 Bq / 20 µL, respectively.

table 12: results testing of spike after micro-precipitation

sample	A [Bq/ 20µL]	± 1σ	yield	± 1σ
^{242}Pu_01	0.07226	0.00770	0.754	0.153
^{242}Pu_02	0.06968	0.01202	0.727	0.178

5.1.2 Preliminary tests for Uranium

Preliminary tests were conducted according to 3.2. The analyzed samples were water from Jachimov, Czech Republic (Jach1, 2, 3), artificial sea water (kMeer1, 2, 3) and Vienna tap water (TW1, 2, 3). Values were corrected using the blank data. Measurement times were 252,000 s for the blanks and varied between 164,523 s and 504,000 s for the samples. The low uranium concentrations in tap water required longer measurement times. A detailed list of measurement times for preliminary tests is listed in the annex.

The first analysis of artificial sea water using method 3 showed lower ^{238}U content than the other two methods and so the same sample preparation was done twice, but the heating time

was more than doubled in the second try. The samples were called kMeer3A (first trial) and kMeer3B (second trial).

table 13: results for preliminary tests method 1

sample	isotope	A_s [Bq / L]	± 1σ	m [µg]	± 1σ
Jach1	U-234	0.20014	0.01454		
	U-238	0.12678	0.00928	10.31	0.92
TW1	U-234	0.00670	0.00070		
	U-238	0.00343	0.00042	0.28	0.15
kMeer1	U-234	0.06373	0.00422		
	U-238	0.07059	0.00464	5.74	0.68

table 14: results for preliminary tests method 2

sample	isotope	As [Bq/L]	± 1σ	m [µg/L]	± 1σ
Jach2	U-234	0.14691	0.00986		
	U-238	0.11500	0.00774	9.35	0.87
TW2	U-234	0.00300	0.00057		
	U-238	0.00291	0.00056	0.24	0.14
kMeer2	U-234	0.06777	0.00596		
	U-238	0.07848	0.00517	6.38	0.72

table 15: results preliminary tests method 3

sample	isotope	A_s [Bq / L]	± 1σ	m [µg]	± 1σ
Jach3	U-234	0.07703	0.00523		
	U-238	0.06328	0.00431	5.14	0.35
TW3	U-234	0.00660	0.00058		
	U-238	0.00361	0.00057	0.29	0.05
kMeer3A	U-234	0.04420	0.00317		
	U-238	0.04744	0.00306	3.86	0.25
kMeer3B	U-234	0.05709	0.00476		
	U-238	0.06147	0.00408	5.00	0.64

table 16: chemical yields in preliminary tests for uranium

sample	chemical yield	± 1σ
Jach1	0.628	0.116
kMeer1	0.379	0.070
TW1	0.517	0.098
Jach2	0.852	0.105
kMeer2	0.334	0.040
TW2	0.453	0.050
Jach3	0.968	0.142
kMeer3A	0.835	0.112
kMeer3B	0.440	0.062
TW3	0.601	0.080

Water from Jachimov showed, as expected, higher ^{238}U contents, ranging from 5.14 µg ^{238}U / L to 10.31 µg ^{238}U / L. This is due to the fact that in this region of the Czech Republic, pitchblende is found. Pitchblende ore mainly consists of U_3O_8 and shows extraordinarily high uranium content of 60 – 90 % [1]. The mass of ^{238}U obtained in the third method was lower (5.14 µg) than for the other two tests, but this result can probably be improved by applying a longer heating time, as it was done for artificial sea water (kMeer3A and kMeer3B).

Uranium content measured in tap water was low, but the obtained data was very consistent and showed little variation (0.24 µg / L, 0.28 µg / L and 0.29 µg / L).

In the first trial of method 3 for artificial sea water, the detected ^{238}U content was significantly lower (3.86 µg / L) than the one found using method 1 and 2 (5.74 and 6.38 µg of ^{238}U per liter). This is why method 3 was done again (kMeer3B), but heating time was more than doubled from 2.5 hours to 6.5 hours. This proofed to be effective, because in this trial, the detected ^{238}U content was higher (5.00 µg / L).

Even though the added amount of ^{238}U solution corresponded to a mass of 3 µg/L, the detected ^{238}U contents were in the range of 5.00-6.38 µg/L. The reason is probably that the actual concentration of this spike solution had also increased due to evaporation of the acid in which it is stored, just like in the case of the ^{242}Pu tracer solution.

Eventually, method 3 of the preliminary tests, including the longer heating period, was chosen for application on the real samples.

5.1.3 Preliminary tests for Uranium and Plutonium

Preliminary tests were carried out according to 3.3.3 and 3.3.4. For the first method, both Vienna tap water and artificial sea water were analyzed, for the second method, only tap water was analyzed.
Measurement times are listed in the attachment.

table 17: results preliminary tests Pu and U first method

sample	isotope	As [Bq/L]	±1σ	yield	±1σ
kMeer_01	Pu-242	0.06459	0.00692	0.674	0.072
	U-234	0.11070	0.00958		
	U-238	0.12719	0.01095		
	U-232			0.163	0.022
TW_01	Pu-242	0.05408	0.00936	0.565	0.098
	U-234	0.01346	0.00113		
	U-238	0.00495	0.00050		
	U-232			0.567	0.026

table 18: results preliminary tests Pu and U second method

sample	isotope	As [Bq/L]	±1σ	yield	±1σ
TW_02	Pu-242	0.06702	0.01157	0.700	0.121
	U-234	0.00339	0.00050		
	U-238	0.00147	0.00065		
	U-232			0.949	0.127

As described in 3.3.5, the second method was chosen for application on real samples, because it was less prone to contamination and produced spectra with better energy resolution. Chemical yields were exceptionally good for the second method, with yields of 70 % for plutonium and 94.9 % for uranium. Fears that the additional step for the plutonium separation may cause a decrease in the yield of the following uranium detection were therefore unfounded.

5.1.4 River and sea water samples

The measurement time was 300,000 s for all samples and the blank. The blank volume was 1,000 mL and the sample volumes varied between 981 mL and 1,471 mL.

table 19: results river and sea water samples α-spectrometry

sample	isotope	As [Bq / L]	± 1σ	m [µg / L]	± 1σ	$^{234}U/^{238}U$	± 1σ
La Palma	U-234	0.05101	0.00378				
	U-238	0.04740	0.00352	3.85	0.56	1.076	0.070
Hawai	U-234	0.03731	0.00260				
	U-238	0.03549	0.00232	2.89	0.40	1.051	0.051
Black Sea	U-234	0.02645	0.00169				
	U-238	0.02280	0.00134	1.85	0.32	1.160	0.035
Irish Sea	U-234	0.03275	0.00276				
	U-238	0.03009	0.00256	2.45	0.45	1.088	0.044
Danube A	U-234	0.01080	0.00098				
	U-238	0.00703	0.00177	0.57	0.22	1.537	0.013
Danube B	U-234	0.01354	0.00147				
	U-238	0.00996	0.00126	0.75	0.24	1.359	0.017
Rio Negro	U-234	< 0.00033					
	U-238	< 0.00029		< 0.02			

table 20: chemical yields in alpha measurements of uranium for sea and river water samples

sample	yield	± 1σ
La Palma	0.355	0.045
Hawaii	0.553	0.096
Black Sea	0.479	0.052
Irish Sea	0.252	0.038
Maliuc A	0.303	0.053
Maliuc B	0.679	0.090
Rio Negro	0.480	0.052

Results for uranium isotopes measured by alpha spectrometry clearly show that ocean water has higher uranium content than river water. ^{238}U contents of sea water samples vary between 3.85 µg / L and 1.85 µg / L, which corresponds to specific activities of 0.0474 Bq / L and 0.0228 Bq / L for ^{238}U and 0.05101 Bq / L and 0.02645 Bq / L for ^{234}U. These values agree well with data in literature which suggest a uranium content of approximately 3 µg / L for sea water [33].
River water (Maliuc, Danube), on the other hand, showed only 0.75 µg and 0.57 µg of ^{238}U per liter, reflecting specific activities of 0.00924 Bq / L for ^{238}U and 0.01256 Bq / L for ^{234}U.
The $^{234}U/^{238}U$ ratio varied between 1.051 for the sample from Hawaii and 1.537 for water from the Danube.

Danube water from Maliuc was analyzed twice, because the chemical yield of the first experiment (30.3 %) was not satisfying and there was enough of the sample left to repeat the procedure. The chemical yield improved in the second try (67.9 %). Results for the activity concentrations and mass of ^{238}U of the two trials correspond sufficiently, considering the fluctuations in natural samples (water was taken from 2 different bottles).

Water from Rio Negro was analyzed three times, but no uranium could be detected. The uranium content was lower than the detection limit of 0.00033 Bq for ^{234}U and 0.00029 Bq for ^{238}U. One of the empty bottles was then filled with 1 M HNO_3 and left for 2 weeks in order to redissolve uranium that may have attached to the walls. The acid solution was then treated like the other water samples, but this attempt was also futile.
The reason for this failure could not clearly be established, but the fact that samples were not acidified shortly after collection might play a role.

The water samples had been collected 2 to 4 years prior to processing and were not acidified at the time of sampling. This may lead to problems in the accurate detection. However, results seem to be consistent, with the exception of water from Rio Negro, in which no uranium was detected by alpha spectrometry. The long storage without acidification may have provoked this failure. In the laboratory, samples were acidified several days or even weeks before further treatment and shaken thoroughly. This approach seems to be successful, apart from the one sample of Rio Negro water.

It is important to acidify water samples soon after sampling, because it was found that acidified water samples show good results for uranium detection even after several years of storage [34].

The problems encountered during the detection of uranium in water from Rio Negro may also be caused by other factors. Water from the Rio Negro is murky and suspended particles could affect measurement. Water from Rio Negro was analyzed twice after filtering off the suspended particles and once without filtration, but in both cases, no uranium was detected.

5.2 AMS results

5.2.1 Introduction

The samples were treated according to 3.4.4. The $^{236}U/^{238}U$ and $^{240}Pu/^{239}Pu$ isotopic ratios were explored.

5.2.2 Results for blanks ($^{236}U/^{238}U$)

table 21: uranium results blanks

sample	$^{236}U/^{238}U$	± 1σ
blank_02	$< 5x10^{-12}$	$1.03x10^{-8}$
blank_03	$1.82x10^{-8}$	$1.21x10^{-8}$
NH_3 blank	$< 5x10^{-12}$	$1.36x10^{-8}$

In the AMS measurements of the blanks, no ^{236}U counts were detected for blank_02 and the NH_3 blank. The detection limit for VERA is $5 \cdot 10^{-12}$ in measurements of the $^{236}U/^{238}U$ ratio [30]. Blank_03 showed ^{236}U counts, but the uncertainty of the $^{236}U/^{238}U$ ratio is significant. For blank_02, 2 L of millipore® water were used, whereas in the case of blank_03, 2 L of bidistilled water were analyzed. As blank_02 showed better results (less ^{236}U counts), only millipore® water was used for all dilutions and other procedures in the sample preparation.

5.2.3 AMS Uranium results

table 22: uranium results water samples

sample	$^{236}U/^{238}U$	± 1σ
La Palma	$1.87x10^{-9}$	$5.62x10^{-10}$
Rio Negro	$2.73x10^{-8}$	$3.26x10^{-9}$
Danube	$1.08x10^{-8}$	$2.64x10^{-9}$
Hawaii	$5.74x10^{-9}$	$3.07x10^{-10}$
Irish Sea	$2.04x10^{-6}$	$2.07x10^{-8}$
Black Sea	$3.63x10^{-9}$	$4.89x10^{-10}$

AMS results for uranium isotopic composition showed that all samples were probably affected by human activity. This is indicated by an atomic ratio $^{236}U/^{238}U$ higher than 10^{-9}. All samples seem to be affected by global fallout and for water from the Irish Sea, an influence of the Sellafield reprocessing plant is obvious.

Furthermore, river samples seem to show higher results for the $^{236}U/^{238}U$ ratio in general, which might be due to the fact that ^{236}U scatters more easily in the huge water volumes of the oceans than it does in rivers and creeks.

table 23: uranium results redissolved filters

sample	$^{236}U/^{238}U$	± 1σ
Jach 1	$2.73x10^{-8}$	$4.15x10^{-9}$
Jach 3	$4.79x10^{-9}$	$1.68x10^{-9}$
TW 3	$2.99x10^{-8}$	$2.59x10^{-8}$
kMeer_01	$2.56x10^{-9}$	$2.22x10^{-9}$
^{232}U_01	$5.58x10^{-8}$	$9.18x10^{-9}$

Some of the filters measured by α-spectrometry were redissolved in order to measure the $^{236}U/^{238}U$ ratio by AMS. Those samples also showed influence by human activity.

5.2.4 AMS Plutonium results

table 24: AMS plutonium results

sample	^{239}Pu counts	^{240}Pu/^{239}Pu	± 1σ
La Palma	27	0.117	0.05
Rio Negro	41	0.086	0.035
Danube	14	0.109	0.069
Hawai	3	0.192	0.222
Irish Sea	18082	0.184	0.003
Black Sea	8	0.253	0.155
blank 02	8	0.199	0.122
blank 03	3	0.177	0.204

Table 24 shows the results of the AMS measurements for ^{239}Pu counts and the isotopic ratio ^{240}Pu/^{239}Pu.

For most samples, the measured ^{240}Pu/^{239}Pu ratios seem to coincide with typical values for global fallout (0.178 ± 0.025 [19]), but due to the low count rates, uncertainties are very high.

Water from the Black Sea showed a higher ^{240}Pu/^{239}Pu ratio of 0.253 ± 0.155, which is probably due to the Chernobyl accident. Releases from the Chernobyl accident are characterized by a ^{240}Pu/^{239}Pu ratio of 0.38 ± 0.07 [19]. Since the 26 April 1986 Chernobyl disaster, the Black Sea has been a sink for Chernobyl-associated radionuclides and is one of the most contaminated marine basins in the Northern Hemisphere [35].

^{239}Pu counts were exceptionally high for Irish Sea water with a total of 18082 counts, which can be attributed to the Sellafield reprocessing plant.

For all other samples, longer measurement times are necessary in order to obtain reliable data.

6 Future Prospects

Further measurements are necessary to obtain more information on the worldwide ^{236}U inventory. ^{239}Pu and ^{240}Pu isotopes are well investigated in solid samples like ores, rocks or corals. Data for sea water, on the other hand, is scarce and more research is needed in this field. The main problem is that plutonium content of sea water is very low and requires high-performance mass spectrometric methods such as accelerator mass spectrometry (AMS).
For the measurement of ^{236}U, AMS is always required, regardless of the sample type. This is why up to date no wide spread studies have been done for the assessment of the ^{236}U inventory.

Further data for ^{236}U / ^{238}U and ^{240}Pu / ^{239}Pu isotopic ratios could provide interesting details on the sample origin and history. As previously mentioned, these isotopic compositions give valuable information on the neutron flux to which a sample was exposed and therefore the sample`s history can be reconstructed. This approach can be useful for a wide range of applications, e. g. in the field of monitoring legal or illicit nuclear activity, where effluents from nuclear power plants and reprocessing facilities could be checked.

In the sampling of water, greater care should be taken to acidify the samples as soon as possible in order to prevent troubles during the sample preparation and detection.

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10 Attachment

10.1 UTEVA® resin

UTEVA® resin (**U**ranium and **TE**tra**V**alent **A**ctinides) was used for extraction of uranium. This resin can be employed for a multitude of different analytical problems, such as uranium measurements in environmental samples, sample preparation of high uranium content samples prior to analysis for other elements, the sequential determination of uranium, plutonium and americium, the measurement of actinides in urine, and the measurement of actinides in high level waste [21].

The functional extractant coated on the inert surface is Dipentyl pentylphosphate, which is shown in figure 5.

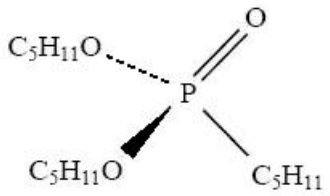

figure 5: Dipentyl pentylphosphate

Dipentyl pentylphosphate shows an affinity for nitrato complexes of uranium (VI), thorium (IV), neptunium (IV) and plutonium (IV). The formation of these complexes depends on the nitrate concentration of the sample solution and the uptake is most efficient at high acid concentrations [36]. This fact is shown in figure 6, where k´ designates the capacity factor.

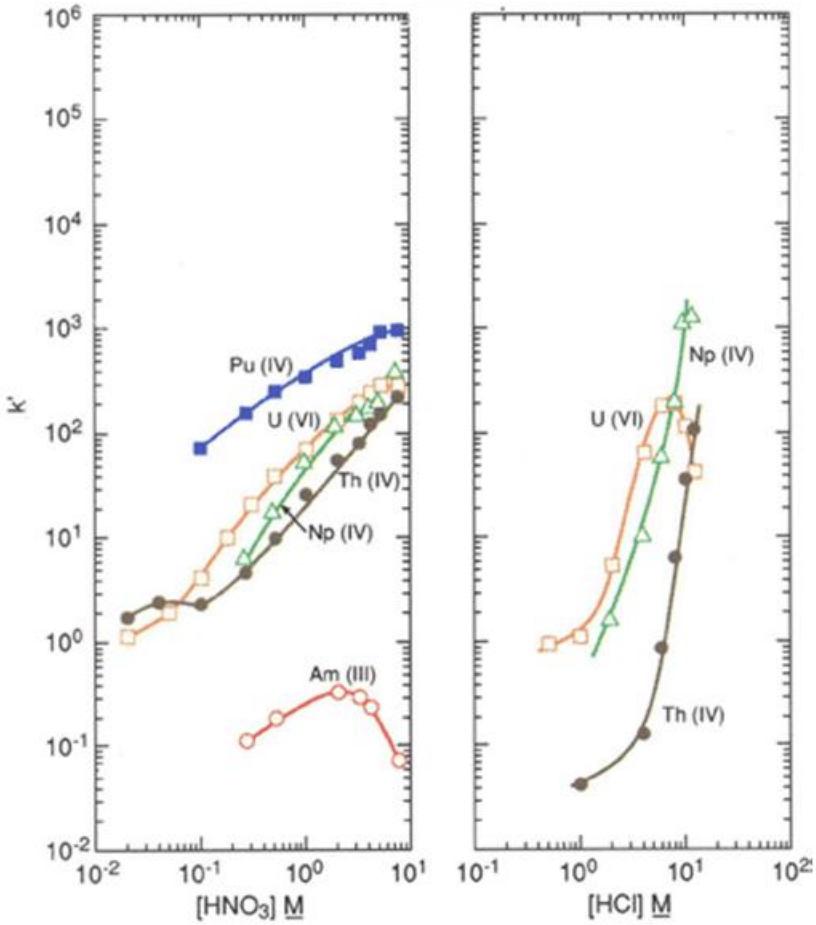

figure 6: Acid dependency of k´ for actinide ions at 23-25°C [37]

The theoretical maximum loading capacity of UTEVA® resin is approximately 37 mg uranium per mL of resin bed. The bed density of UTEVA® resin is 0.39 g/mL [36].

10.2 Preparation of solutions

10.2.1 Calculation of ^{238}U spike addition for artificial sea water:

It was taken into account that literature suggests a uranium content in sea water of about 3 µg/ L [24] and therefore, ^{238}U spike solution was added to artificial sea water. The calculation was done as follows:

Activity of the ^{238}U spike solution was 17.6 Bq / mL.

Multiplication of the decay constant λ with the number of atoms N gives the activity A:

$$A = \lambda \cdot N$$

The decay constant was calculated using the half life of ^{238}U ($4.5 \cdot 10^9$ a):

$$\lambda = \frac{\ln 2}{\tau_{1/2}} = \frac{\ln 2}{4.5 \cdot 10^9 \cdot 365 \cdot 24 \cdot 3600 s} = 4.88 \cdot 10^{-18} s^{-1}$$

Next, the atomic number of one milliliter of spike solution was calculated:

$$N = \frac{A}{\lambda} = \frac{17{,}6 Bq}{4{,}88 \cdot 10^{-18} s^{-1}} = 3{,}61 \cdot 10^{18}$$

The mass m of one milliliter of spike solution is then calculated with the following formula:

$$N = \frac{m}{M} \cdot N_L \qquad m = \frac{N \cdot M}{N_L} = \frac{3.61 \cdot 10^{18} \cdot 238 g mol^{-1}}{6.022 \cdot 10^{23} mol^{-1}} = 1.4 \cdot 10^{-3} g = 1.4 mg$$

M .... atomic mass [g/mol]

N_L .... Avogadro constant ($6.002 \cdot 10^{23}$ mol^{-1})

1 L of artificial sea water was prepared, therefore, 3 µg of ^{238}U were needed. As 1 mL corresponds to 1.4 mg ^{238}U, 2.1 µL were added to obtain the desired 3 µg ^{238}U per liter of artificial sea water.

10.2.2 Mixing of $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$

1.25 M $Ca(NO_3)_2$ and 3.2 M $(NH_4)_2HPO_4$ solution were prepared for usage in preliminary method number 2. The solutions were made by mixing the solid salts in millipore® water.
1.25 M $Ca(NO_3)_2$ solution was mixed from $Ca(NO_3)_2 \cdot 4H_2O$ salt with an atomic mass of M = 236.15 g mol^{-1} and 3.2 M $(NH_4)_2HPO_4$ solution from the $(NH_4)_2HPO_4$ salt with an atomic mass of M = 132.06 $gmol^{-1}$. 100 mL of 1.25 M $Ca(NO_3)_2$ and 10 mL of 3.2 M $(NH_4)_2HPO_4$ solution were prepared.
Two simple formulae were used:

$$n = \frac{m}{M} \qquad c = \frac{n}{V}$$

c .... concentration [g / L]

V .... volume [L]

First, the amount of substance n [mol] for 1.25 M $Ca(NO_3)_2$ solution was calculated:

$$n = c \cdot V = 1.25 mol/L \cdot 0.1 L = 0.125 mol$$

Next, the mass of salt needed for 100 mL of solution was obtained by multiplying n with the atomic mass M:

$$m = n \cdot M = 0.125 mol \cdot 236.15 g/mol = 29.52 g$$

Calculations for the 3.2 M $(NH_4)_2HPO_4$ solution were done in the same way:

$$n = c \cdot V = 3.2 mol/L \cdot 0.01 L = 0.032 mol$$

$$m = n \cdot M = 0.032 mol \cdot 132.06 g/mol = 4.2 g$$

In conclusion, 29.52 g of $Ca(NO_3)_2$ and 4.2 g of $(NH_4)_2HPO_4$ were diluted in 100 mL and 10 mL flasks respectively, to achieve 1.25 M $Ca(NO_3)_2$ and 3.2 M $(NH_4)_2HPO_4$ solutions.

10.3 Evaluation

10.3.1 LSC

The activity concentration of the ^{242}Pu tracer was verified using liquid scintillation spectrometry. LSC registered 29.025 cpm (counts per minute) with an error of 1.485 cpm for the spike solution and 0.287 cpm with an uncertainty of 0.148 cpm for the blank.

First, the counts per second were calculated:

$$cps = \frac{cpm}{60} = \frac{29.025}{60} = 0.484 cps$$

The counts per second of the error were calculated in the same way:

$$cps_\sigma = \frac{cpm}{60} = \frac{1.485}{60} = 0.02475 cps$$

The data of the blank is treated in the same way:

$$cps = \frac{cpm}{60} = \frac{0.287}{60} = 0.00478 cps$$

$$cps_\sigma = \frac{cpm}{60} = \frac{0.148}{60} = 0.002467 cps$$

Next, the activity concentration can be calculated:

$$A(Bq) = \left(cps_{spike} - cps_{blank}\right) \pm \left(\sqrt{\sigma_{spike}^2 + \sigma_{blank}^2}\right)$$

$$A = \left(0.484 - 0.00478\right) \pm \sqrt{0.002475^2 + 0.002467^2} = \left(0.479 \pm 0.0249\right) Bq / 100 \mu L$$

The added tracer volume was always 20 µL. The corresponding activity concentration is 0.0985 ± 0.0049 Bq / 20 µL (October 11, 2011).

10.3.2 Alpha spectrometry

In this section, the evaluation of alpha spectra is discussed.

10.3.2.1 Activity concentration of the tracer

The time elapsed since the activity concentration of the spike was measured and the spike labeled has to be considered in order to obtain the actual value of the activity concentration at the time of measurement of the sample. The reference date for the ^{232}U spike was 09/30/2005 and at that time, activity concentration was attested to be 0.0289 ± 0.0018 Bq / 20 µL. As samples were measured on different days, the correction for the elapsed time had to be done individually for each sample.

As an example, the calculation is done for the La Palma sample, which was measured on 11/26/2010. The elapsed time is 1883 days, but has to be converted into seconds:

$$t_{elapsed}(s) = t(d) \cdot 24 \cdot 3600 = 1883 \cdot 24 \cdot 3600 s = 162{,}691{,}200 s$$

The half-life of ^{232}U is 72 years, which is also converted into seconds.

$$\tau_{1/2}(s) = 72 \cdot 365 \cdot 24 \cdot 3600 = 2{,}270{,}592{,}000 s$$

With the help of the half-life, the decay constant of ^{232}U is calculated:

$$\lambda = \frac{\ln 2}{\tau_{1/2}} = 3.053 \cdot 10^{-10} s^{-1}$$

The activity concentration at the time of measurement is obtained through the following step:

$$A(Bq) = A_0 e^{-\lambda \tau_{1/2}} = 0.0275 Bq$$

10.3.2.2 Activity concentrations

For the counts shown in the alpha spectra, the measurement time has to be accounted for:

$$cps = \frac{counts}{t_M}$$

cps .... counts per second

t_M .... measurement time

Thus, the counts per second can be calculated for both the sample and the blank.

Next, the cps of the blank are subtracted from the cps of the sample. This value is then multiplied with the measurement time of the sample to obtain the actual counts.

$$counts_{sample-blank} = (cps_{sample} - cps_{blank}) \cdot t_M$$

This allows assessment of the activity concentration of the spike (^{232}U, ^{242}Pu) in the next step. This is not the theoretical activity concentration of the spike, but the activity concentration measured.

$$A(spike) = \frac{counts_{sample-blank}}{\varepsilon \cdot t_M}$$

ε .... detector efficiency

For evaluation of ^{234}U and ^{238}U activity concentrations, another formula was used. The counts are blank-corrected and A_{th} is the theoretical activity concentration of the spike solution.

$$A = \frac{counts}{counts_{spike}} \cdot A_{th}$$

10.3.2.3 Chemical yield

The proportion of the measured activity concentration and the theoretically expected activity concentration of the spike is calculated to obtain the chemical yield.

$$yield = \frac{A_{measured}}{A_{theoreticd}}$$

10.3.2.4 Mass of ^{238}U

For calculation of the mass of ^{238}U [µg], the activity concentration in mBq was divided by 12.3 to obtain the mass of ^{238}U [µg].

$$m(^{238}U) = \frac{A(mBq)}{12.3(mBq/\mu g)}(\mu g)$$

10.4 Calculation of uncertainties

Errors for the counts of both sample and blank are expressed by the square root of the respective counts:

$$\sigma_{cts} = \sqrt{counts}$$

The counts are designated by cts.

Errors of the blank-corrected counts are calculated in the following way:

$$\sigma_{cts(sample-blank)} = \sqrt{\sigma^2_{cts(sample)} + \sigma^2_{cts(blank)}} \cdot t_M$$

Error for the activity concentration of the spike ^{232}U is obtained with the following formula:

$$\sigma_A = \frac{\sqrt{\left(\frac{1}{\varepsilon}\right)^2 \cdot \sigma^2_{cts} + \left(\frac{counts}{\varepsilon^2}\right)^2 \cdot \sigma^2_{\varepsilon}}}{t_M}$$

The uncertainties for the activity concentrations of the ^{234}U and ^{238}U isotopes, on the other hand, have to be calculated in another way.

$$\sigma_A = \sqrt{\left(\frac{cts_{sample}}{cts_{spike}}\right)^2 \cdot \sigma^2_{A_{spike}} + \left(\frac{A_{spike}}{cts_{spike}}\right)^2 \cdot \sigma^2_{cts_{sample}} + \left(\frac{A_{spike} \cdot cts_{sample}}{cts^2_{spike}}\right) \cdot \sigma^2_{cts_{spike}}}$$

Uncertainty of the chemical yield:

$$\sigma_y = \sqrt{\left(\frac{1}{A_{theoreticd}}\right)^2 \cdot \sigma^2_{A_{measured}} + \left(\frac{A_{measured}}{A^2_{theoreticd}}\right)^2 \cdot \sigma^2_{A_{theoreticd}}}$$

$A_{theoretical}$ is the theoretical activity concentration of the spike and $A_{measured}$ is the measured activity contenration.

10.5 Detection limit

The detection limit L_D for alpha spectrometry was calculated according to Currie [38], who suggests the following formula:

$$L_D = \left(2.71 + 4.65 \cdot \sqrt{cps_{blank} \cdot t_{M_{sample}}}\right) \cdot \frac{A_{spike}}{cts_{spike}}$$

Table 25 shows the detection limit L_D for samples measured by alpha spectrometry.

table 25: Detection limit in α-measurement

sample	isotope	L_D [Bq]
La Palma	^{234}U	0.00048
	^{238}U	0.00039
Hawai	^{234}U	0.00029
	^{238}U	0.00024
Black Sea	^{234}U	0.00025
	^{238}U	0.00029
Irish Sea	^{234}U	0.00072
	^{238}U	0.00064
Maliuc	^{234}U	0.00029
	^{238}U	0.00024
Rio Negro	^{234}U	0.00033
	^{238}U	0.00029

10.6 Measurement times

table 26: measurement time in preliminary tests for uranium

sample	measurement time [s]
TW1	252,000
kMeer1	252,000
Jach1	164,523
blank1	252,000
TW2	504,000
kMeer2	254,600
Jach2	252,000
blank2	252,000
TW3	504,000
kMeer3A	332,000
kMeer3B	252,000
Jach3	252,000
blank3	252,000

table 27: measurement times in preliminary tests for combined uranium and plutonium detection

sample	isotopes	measurement time [s]
kMeer_01	^{242}Pu	74,003
	^{232}U, ^{234}U, ^{238}U	252,000
TW_01	^{242}Pu	73,907
	^{232}U, ^{234}U, ^{238}U	252,000
TW_02	^{242}Pu	74,002
	^{232}U, ^{234}U, ^{238}U	300,000

For river and sea water samples, the measurement time was always 300,000 s.

10.7 Budis Mineral Water

During the preliminary tests, Budis mineral water from Slovakia was analyzed.
First, the sample was acidified and 20µL of ^{232}U spike (0.0289 ± 0.0018 Bq/ 20µL; September 30, 2005) were added. After the sample volume of 2,930 mL was evaporated to approximately 1 L, the sample was treated according to method number 2 of the preliminary tests for uranium separation (see 3.2.3).

table 28: alpha results uranium activity concentrations of Budis Mineral Water

isotope	As [Bq / L]	± 1σ	m [µg / L]	± 1σ
U-234	0.02132	0.00154		
U-238	0.00834	0.00064	0.68	0.14

Results for the ^{234}U and ^{238}U activity concentrations from alpha spectrometry were used to check whether the recommended indicative dose for drinking water was exceeded. The WHO recommended in 2004 a maximum annual indicative dose of 24 µSv/a for ^{234}U and ^{238}U, which corresponds to 185 mBq/L for ^{238}U or a content of 15 µg/L of natural uranium.

The annual effective dose is calculated by multiplication of the activity concentration, the annual consumption (V) of mineral water and the dose conversion factor (f).

$$dose(Sv/a) = A_s(Bq/L) \cdot V(L/a) \cdot f(Sv/Bq)$$

The dose conversion factors f (Sv/Bq) for babies and teens are higher than those for adults. For babies, the worst case scenario was presumed, meaning that the entire water consumption of 170 L per year is based on mineral water. The annual consumption of mineral water for teens and adults is approximately 100 L.

table 29: annual indicative dose from uranium isotopes in Budis mineral water

age group	isotope	As [Bq / L]	V (L/a)	f (Sv/Bq)	dose (µSv/a)
babies	U-234	0.02132	170	3.70E-07	1.34
	U-238	0.00834	170	3.40E-07	0.48
teens	U-234	0.02132	100	7.40E-08	0.16
	U-238	0.00834	100	6.80E-08	0.06
adults	U-234	0.02132	100	4.90E-08	0.10
	U-238	0.00834	100	4.50E-08	0.04

For Budis mineral water, the annual indicative dose from ^{234}U and ^{238}U is not exceeded for any of the age groups.

The filter from alpha spectrometry of Budis mineral water was redissolved in order to measure the $^{236}U/^{238}U$ ratio by AMS.

table 30: AMS results Budis mineral water

sample	$^{236}U/^{238}U$	± 1σ
Budis	2.17×10^{-8}	6.55×10^{-9}

10.8 Proficiency test IAEA-CU-2010-04 ALMERA

In the course of my diploma work, I also participated in the IAEA-CU-2010-04 ALMERA proficiency test on the determination of natural radionuclides in water. Three spiked water samples were analyzed regarding their ^{234}U and ^{238}U activity concentrations. The samples sent by the IAEA were treated according to the procedures of the first method of the preliminary tests for uranium separation (see 3.2.1) and measured by alpha spectrometry. The samples were split into 2-4 fractions and the average concentrations of uranium isotopes were calculated. Sample 1 was split into 2 fractions (S01A, S01B), sample 2 into 4 fractions (S02A, S02B, S02C, S02D) and sample 3 into 3 fractions (S03A, S03B, S03C).

table 31: results sample 2 proficiency test

sample 2	volume [mL]	A [Bq/L] ^{234}U	± 1σ	A [Bq/L] ^{238}U	± 1σ
S02A	100	1.04315	0.07140	0.55375	0.03480
S02B	100	0.89298	0.06280	0.47761	0.03401
S02C	50	1.07227	0.08056	0.60667	0.04079
S02D	50	1.11220	0.09700	0.65213	0.05478
average		1.03015	0.09573	0.57254	0.07498

table 32: results sample 3 proficiency test

sample 3	volume [mL]	A [Bq/L] ^{234}U	± 1σ	A [Bq/L] ^{238}U	± 1σ
S03A	50	0.32196	0.02346	0.21012	0.01581
S03B	50	0.33400	0.02519	0.23156	0.01801
S03C	51	0.35363	0.02696	0.22386	0.01670
average		0.33653	0.01599	0.22185	0.01086

Results for sample 2 and 3 of the proficiency test are shown in table 32 and 33 respectively. For sample 1, no ^{234}U or ^{238}U was detected. Sample 2 and 3 showed high uranium contents. For example, an average ^{234}U activity concentration of 1.0 Bq / L was established for sample number 2.

For determination of the average activity concentration, the arithmethic mean was calculated. The standard deviation of the average activity concentration was calculated according to the following formula:

$$s = \sqrt{\frac{1}{n-1} \cdot \sum (x - \bar{x})^2}$$

Table 33 shows the chemical yields of all samples analyzed in the course of the proficiency test.

table 33: chemical yields of samples in proficiency test

sample	yield	± 1σ
S01A	0.901	0.165
S01B	0.882	0.153
S02A	0.964	0.141
S02B	0.915	0.169
S02C	0.618	0.069
S02D	0.767	0.134
S03A	0.937	0.117
S03B	0.984	0.147
S03C	0.761	0.084

11 Curriculum Vitae

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