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Determination of Ra-226 in Environmental Samples using ICP-QQQ after Cation Exchange-Separation

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Abstract

The goal for this master project was to develop a method to determine the content of ^{226}Ra in environmental samples using triple quadrupole Inductively Coupled Plasma Mass Spectrometry. It was desirable to develop an applicable method to various types of samples with different types of matrices, e.g. freshwater, produced water and soil. The goal for the procedure was to avoid coprecipitation with $BaSO_4$, and matrix problems in the procedure, and being less time-consuming if there is an urgent need for results. It was desirable to measure the samples using ICP-QQQ-MS (Agilent 8800 ICP-MS triple quadrupole), measuring on mass-to-charge ratio instead of emitted radiation. The speciation of ^{226}Ra, which means different forms of ^{226}Ra, was not taken into account.

^{226}Ra is one of four isotopes of radium, and is considered a highly radiotoxic isotope. Thus, there is a need for determination of ^{226}Ra in the environment. Long-time exposure can lead to harmful effects such as anemia, fractured teeth, various types of cancer and death (ATSDR. 1999). Today, many methods can be applied to determine the concentration of the radioactive isotope ^{226}Ra. The methods are based on different chemical and physical principles, and the reachable detection limits, selectivity and reproducibility differ between the methods. A study performed by Köhler et al. in 2001 compared the different methods for the analysis of ^{226}Ra in water samples. The study showed that the methods differed in duration of complete analysis, combined uncertainties, blank count rate and sensitivity. All of these parameters are important to consider when choosing a method to determine the concentration of ^{226}Ra in environmental samples.

In a study performed by Kim et al. in 1999, determined ^{226}Ra in groundwater and soil by using high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS). The procedure for quantifying ^{226}Ra in environmental samples in this thesis has taken the article and study by Kim et al., called "*Determination of ^{226}Ra in Environmental Samples using High-Resolution Inductively Coupled Plasma Mass Spectrometry*", into account and optimized it further for the use in the Isotope Laboratory, Norwegian University of Life Sciences at Ås (Kim et al. 1999).

Various types of environmental samples were prepared by the developed procedure. The samples had different matrices, and the environmental samples included freshwater from Orrefjell, produced water from Troll C (salinity of 4.8% (w/V)), and soil samples from Orrefjell. By testing different types of samples, it was possible to determine if the method was applicable to various types of matrices – which was desirable. ^{133}Ba was used as both yield monitor and internal standard, measured on NaI and ICP-MS.

Prior to measurement of environmental samples containing ^{226}Ra, recovery- and spiking tests were performed. The gamma-emitter, ^{133}Ba, with known concentration was added to water samples without any sample matrix at the beginning of the sample preparation. 1 mL of ^{133}Ba with a concentration of 9.30 ng/L (88.0 Bq/mL) was added to a two liter sample of DI-water. After each step of the ion exchange-procedure the solutions were measured by a NaI-detector to determine the loss of ^{133}Ba in each specific stage of the sample preparation. The disintegration per minute (DPM) from the measurements were compared to a reference solution, containing the same concentration of ^{133}Ba as added to the sample. The reference solution of ^{133}Ba was measured directly on NaI-detector after preparation. By comparing the presence of ^{133}Ba in each solution to the reference, it was possible to detect the critical stages of the ion exchange-procedure – and correct for the loss of ^{133}Ba, and the

analyte ^{226}Ra. These tests were performed for all prepared samples presented in this thesis. To consider whether the procedure was optimal and well-functioning for its purpose, it was concluded that a recovery of at least 70% would be sufficient. The recovery tests were used to determine optimal flow rate of acids used for ion exchange separation. A flow rate of 1.6-2.0 mL/min was concluded as optimal flow rate. The article published by Kim et al. from 1999, used a flow rate of 2 mL/min during the ion exchange separation.

The average recovery of ^{133}Ba was determined to be 81 ± 6.1% for both spiked samples and freshwater samples from Orrefjell. Produced water samples with a salinity of 4.8% (w/V) had an average recovery of 57 ± 5.3% (Mekhonina, V. 2017). Hence, the assumption was correct – a more complex matrix influences the recovery of the yield monitor.

The soil samples needed preparation prior to ion exchange-separation. It was desirable to find the optimal digestion technique using microwave digestion (UltraCLAVE IV from Milestone Inc) and acid dissolution. Barium, and radium, will be almost insoluble when bound as sulphates, so the focus was to determine the optimal digestion of barium bound as barium sulphate. Even though barium is slightly less stable than radium when present as sulphates, the recovery of barium after digestion was expected to be lower than for radium. This is explained by the fact that barium sulphate will be present in the soil in a much greater amount than radium sulphates. Several certified reference materials were tested with different acid solutions to find the optimal technique with good recovery of barium. A combination of phosphoric acid and nitric acid digested for 40 minutes at 260°C proved to give the best recovery for barium as well as for rare earth elements. The average recovery of ^{133}Ba in soil samples after ion-exchange was 62 ± 36% if soil sample 4.1 and alum shale was included. These two samples had a recovery of 4.9% and 5.7% respectively for soil sample 4.1 and alum shale, which greatly affected the average value and standard deviation. If these two samples were excluded, the average recovery of ^{133}Ba was 81 ± 11%.

The critical steps of the ion exchange-separation were 1.5M ammonium acetate and 3M hydrochloric acid for all environmental samples.

The blank samples for produced water and soil were measured, and used to determine the limit of detection for *both* water- and soil procedure. The limit of detection was determined to be 0.052 pg/L for water procedure, including soil blanks – thus, this is the "worst case scenario"-LOD for water procedure. The LOD for water procedure was below the upper limit set by USEPA – 1 pg ^{226}Ra/L for methods used for analysis of drinking water (Park, Chang J. et al. 1998 The limit of detection for soil samples was determined to be 21 pg ^{226}Ra/kg soil. However, it is believed with a proper clean-up procedure, the limit of detection will decrease for soil samples. The UltraCLAVE-vials, made by TFM, used in this project, have earlier been used for soil samples possibly contaminated with ^{226}Ra – which could have affected the blank values.

Using N_2O as reaction gas excludes interferences from polyatomic masses for ^{226}Ra, and isobaric overlap from ^{133}Cs for ^{133}Ba. It is not a conventional gas mode, but the advantage of measuring the recovery of ^{133}Ba directly on ICP-QQQ compared to NaI-detector, is the possibility to detect matrix effects happening within the ICP-MS. Thus, it was possible to determine the recovery of the ISTD for the full procedure – sample preparation to complete measurement on ICP-QQQ. Eliminating the measurement of the yield monitor on NaI-detector, makes the duration of complete analysis shorter – which is desirable if there is an urgent need for results.

The results from ICP-QQQ, using N_2O as reaction gas and semiconductor lens, showed that the measurements were accurate for spiked water samples. Thus, assuming accurate results for the other freshwater samples as well. Precision could not be determined since no parallel-samples were measured. There was no significance difference between yield- and ISTD-correction of the results for freshwater samples. Thus, both correction-techniques could be used.

The soil samples were diluted and measured with X-lens on ICP-QQQ, and to verify the results, NRPA in Tromsø measured the soil samples by Ge-detector. The Ge- and ICP-MS-measurements, both yield- and ISTD-corrected, were compared to determine whether or not the new procedure was applicable for soil samples. The comparison showed that there was no significance difference between the group means. The p-value given in the output was 0.927, thus, the hypothesis assuming equal population means could not be rejected. The control samples, soil samples from Orrefjell (O1-O3), were not significantly different from the measured value from NRPA, Tromsø – 548 ± 15 Bq/kg compared to 530 ± 0.0 Bq/kg corrected with ISTD, and 520 ± 42 Bq/kg corrected with yield. This indicates that the results of soil samples can be corrected with ^{133}Ba both as yield and ISTD.

However, an aspect of the statistical tests, is the number of samples (N). A small sample number was measured and tested, and several samples should be measured to obtain a more reliable result from the statistical tests. This is an important aspect which regards all statistical tests presented in this thesis.

There are several aspects of the method that should be optimized further. The most important aspect is the choice of yield monitor or internal standard. ^{133}Ba was used in this master project, assuming equal loss of ^{133}Ba and ^{226}Ra. However, the result from the test performed, showed a changing relationship between ^{226}Ra and ^{133}Ba throughout the procedure – ^{226}Ra seemed to have a stronger affinity to the resin. For freshwater samples the ratio (cps ^{226}Ra/ cps ^{133}Ba) changed from 33% to 43% during sample preparation, and it is assumed that the ratio is affected even more with more complex matrix. A changing relationship indicates unequal behavior between yield monitor/ISTD and analyte, and correcting the loss of ^{226}Ra with the loss of ^{133}Ba should be done with care. However, only one test for freshwater was performed, so this needs to be tested further. Perhaps another internal standard should be considered – Larivière et al. published an article in 2005 were ^{228}Ra was used as yield monitor for soil- and sediment samples (Larivière et al. 2005).

Measurement of ^{226}Ra on ICP-QQQ, as presented in this thesis, can be used for determination of ^{226}Ra in water samples and soil samples. The procedure was not tested for biota samples, but it is desirable to develop the procedure further to make it applicable to biota samples as well. However, the results presented in this thesis are not fully reliable due to a changing relationship between ^{133}Ba and ^{226}Ra, lack of parallels and a small sample number (N). The LOD for water procedure did meet the required upper limit set by USEPA for drinking water analysis.

Sammendrag

Målet for denne masteroppgaven var å utvikle en metode for å bestemme innholdet av isotpoen ^{226}Ra i miljøprøver ved bruk av trippel kvadrupol Inductively Coupled Plasma Mass Spectrometer. Det var ønskelig å utvikle en metode som var brukbar til forskjellige typer prøver med ulik matriks, som for eksempel ferskvann, produsert vann og jord. Målet for prosedyren var å unngå medfelling med $BaSO_4$, ha færre matrikser i prosedyren, og at prosedyren skulle være rask i tidsbruk ved behov for raske resultater. Det var ønskelig å måle prøvene på ICP-QQQ (Agilent 8800 trippel kvadrupol) ved å måle masse-til-ladning (m/z) i stedet for stråling. Spesieringen av ^{226}Ra, som betyr ulike former av ^{226}Ra, ble ikke tatt hensyn til.

^{226}Ra er en av fire isotoper, og er ansett som en radiotoksisk isotop. Derfor er det et behov for å bestemme, samt regulere, ^{226}Ra i miljøet. Eksponering over lang tid kan føre til skadelige effekter som anemi, tannskader, ulike typer kreft og død (ATSDR. 1999). I dag finnes det mange metoder for å bestemme konsentrasjonen av den radioaktive isotopen ^{226}Ra. Metodene baserer seg på ulike kjemiske og fysiske prinsipper, og har ulik deteksjonsgrense, selektivitet og reproduserbarhet. En studie gjort av Köhler et al. fra 2001, sammenlignet ulike analysemetoder for ^{226}Ra i vannprøver. Studien viste at de målte parameterne varierte, som for eksempel tidsbruk, usikkerhet, blankverdier og sensitivitet. Dette er parametere som er viktig å ta i betraktning når det velges metode for å bestemme konsentrasjonen av ^{226}Ra i miljøprøver.

En studie gjort av Kim et al. fra 1999, bestemte ^{226}Ra i grunnvann og jord ved bruk av høyoppløselig induktivt koblet plasma massespektrometer (HR-ICP-MS). Prosedyren brukt for kvantifisering av ^{226}Ra i miljøprøver i denne masteroppgaven har tatt utgangspunkt studien gjort at Kim et al. Prosedyren presentert i artikkelen "*Determination of ^{226}Ra in Environmental Samples using High-Resolution Inductively Coupled Plasma Mass Spectrometry*", har blitt optimalisert for bruken på Isotoplaboratoriet, NMBU Ås.

Ulike typer av miljøprøver ble preparert med den nye prosedyren. Prøvene hadde ulike matrikser, og prøvene inkluderte ferskvann fra Orrefjell, produsertvann fra Troll C (salinitet 4,8%) (Mekonina, V. 2017), samt jordprøver fra Orrefjell. Ved å teste metoden opp mot ulike typer matrikser, var det mulig å bestemme om metoden var brukbar til ulike typer matrikser – som var ønskelig. ^{133}Ba ble brukt som yield monitor og internstandard, og ble målt både på NaI og ICP-MS.

Før prøver med naturlig ^{226}Ra ble preparert, ble gjenvinnings- og tilsetningstester gjort. ^{133}Ba, som avgir gammastråling, ble tilsatt i kjent konsentrasjon/aktivitet til en vannprøve uten matriks ved oppstart av prosedyren. Det ble tilsatt 1 mL 9,30 ng/L (88.0 Bq/mL) ^{133}Ba til to liter vann var rundt 1 mL 9,30 ng/L (88.0 Bq/mL). Etter hvert steg under ionebytteseparasjonen ble løsningene målt på NaI-detektoren for å bestemme tapet av ^{133}Ba i det spesifikke steget. Disintegrasjonene per minutt (DPM-verdiene) fra målingen ble sammenlignet mot en referanseløsning, som innehold den samme konsentrasjonen av ^{133}Ba som tilsatt i prøven. Referanseløsningen av ^{133}Ba ble målt direkte på NaI-detektoren etter tillaging. Ved å sammenligne tilstedeværelsen av ^{133}Ba i hver løsning mot referansen, var det mulig å bestemme de kritiske stegene i ionebytteseparasjonen – og dermed korrigere for tapet av ^{133}Ba, og analytten ^{226}Ra. Dette ble gjort for alle preparerte prøver presentert i denne masteroppgaven. Det ble bestemt at minst 70% gjenvinning av ^{133}Ba vil være nok for å betrakte prosedyren som optimal og velfungerende. Gjenvinningstestene ble brukt til å bestemme optimal strømningshastighet, og en strømningshastighet på 1,6-2,0 mL/min ble ansett som optimalt for syrene brukt i

ionebytteseparasjonen. Artikkelen publisert av Kim et al. fra 1999 brukte en strømningshastighet på 2 mL/min under ionebytteseparasjonen.

Gjennomsnittlig gjenvinning ble 81 ± 6,1% for tilsteningsprøver og Orrefjell ferskvannsprøver. Produsert vann fra Troll C, salinitet på 4,8% (Mekhonina, V. 2017) hadde en gjennomsnittlig gjenvinning på 57 ± 5,3%. Antakelsen om at prøver med mer kompleks matriks har lavere gjenvinning ble ansett som korrekt.

Jordprøvene trengte ytterligere prøveopparbeidelse før ionebytteseparasjonen. Det var ønskelig å finne en optimal oppslutningsmetode ved bruk av mikrobølgeoppslutning (UltraCLAVE IV fra Milestone Inc) og syrer. Barium, og radium, vil nesten alltid være uløselige når de er bundet som sulfater, så fokuset var å finne en optimal oppslutning av barium bundet som bariumsulfat. Selv om barium er mindre stabil enn radium bundet som sulfat, var det antatt at gjenvinning av barium ville være lavere enn for radium. Dette forklares med at bariumsulfat er tilstede i mye større grad i jord sammenlignet med radiumsulfat. Ulike typer sertifiserte referansematerialer ble testet med ulike syreløsninger for å finne den optimale oppslutningen med god gjenvinning av barium. En kombinasjon av fosforsyre og salpetersyre oppsluttet i 40 minutter ved 260°C på UltraCLAVE viste seg å gi best gjenvinning av barium, samt andre sjeldne jordarter. Den gjennomsnittlige gjenvinningen av ^{133}Ba etter separasjonen ved bruk av ionebytter var 62 ± 36%, dersom jordprøve 4.1 og Alunskiferprøven ble inkludert. Disse to prøvene hadde en gjenvinning på 4,9% og 5,7%, henholdsvis for jordprøve 4.1 og Alunskiferprøve, som påvirket den gjennomsnittlige verdien samt standardavviket. Dersom disse to prøvene ble ekskludert, ble gjennomsnittlig gjenvinning av ^{133}Ba, og dermed ^{226}Ra, 81 ± 11%.

De kritiske stegene i ionebytteseparasjonen var 1,5M ammoniumacetat og 3M saltsyre. Dette gjaldt for alle typer miljøprøver.

Blankprøvene for produsert vann og jord ble målt, og brukt til å bestemme deteksjonsgrensen for *både* vann- og jordprosedyre. Deteksjonsgrensen for vannprosedyren ble bestemt til 0,052 pg/L, hvor jordblankene ble inkludert- Altså, illustrerer dette en LOD som er mye høyere enn realiteten. LOD for vannprosedyren var allikevel under enn den øvre grensen satt av USEPA – 1pg ^{226}Ra/L for metoder brukt for å analysere drikkevann (Park, Chang J. et al. 1998). Deteksjonsgrensen for jordprøver ble bestemt til 21 pg ^{226}Ra/kg jord. Det er antatt at en ordentlig vaskeprosedyre vil minke deteksjonsgrensen for jordprøver. UltraCLAVE-rørene laget av TFM, har tidligere blitt brukt til oppslutning av jordprøver som kan ha inneholdt ^{226}Ra, og dette kan ha ført til tellinger i blankprøvene.

Ved bruk av reaksjonsgassen N_2O ekskluderes interferenser fra polyatomiske masser for ^{226}Ra, samt ^{133}Cs for ^{133}Ba. Dette er ikke en konvensjonell reaksjonsgass, men fordelen er at gjenvinningen av ^{133}Ba kunne måles direkte på ICP-QQQ. Ved å måle ^{133}Ba på ICP-QQQ var det mulig å detektere matrikseffekter i selve instrumentet – dette var ikke mulig ved måling på NaI. Det var dermed mulig å bestemme gjenvinningen av hele prosedyren fra start til måling på ICP-MS. Ved å eliminere målingen av ^{133}Ba på NaI-detektoren, blir også tidsbruken på metoden kuttet ned – som kan være ønskelig dersom det er behov for resultater snarest.

Resultatene fra ICP-QQQ ved bruk av N_2O som reaksjonsgass, samt S-linse, viste at målingene var nøyaktige for tilsetningsprøvene. Derfor antas det at resultatene for ferskvannsprøvene fra Orrefjell også er nøyaktige. Presisjonen kunne ikke bestemmes da det ikke ble kjørt paralleller av prøvene. Det var ingen signifikant forskjell mellom yield- og internstandard-korrigering av ferskvannsresultater. Dette betyr at begge korrigeringsteknikkene kan benyttes.

Jordprøvene ble fortynnet og målt med X-linse på ICP-QQQ, og for å verifisere resultatene målte Statens Strålevern i Tromsø jordprøvene ved bruk av en Ge-detektor. Ge-resultatene og ICP-MS-resultatene, både yield- og ISTD-korrigerte, ble sammenlignet for å bestemme om den nye prosedyren var brukbar for jordprøver. Sammenligningen viste at det ikke var signifikant forskjell mellom gruppegjennomsnittene. P-verdien fra den statistiske testen var 0,927, som indikerte at nullhypotesen ikke kan forkastes – H_0: likt gruppegjennomsnitt for gruppene. Kontrollprøvene, jordprøvene fra Orrefjell (O1-O3), var ikke signifikant forskjellige fra referanseverdien målt av Statens Strålevern i Tromsø - 548 ± 15Bq/kg sammenlignet med 530 ± 0 Bq/kg korrigert med ISTD, og 520 ± 42 Bq/kg korrigert med yield.

Et aspekt av de statistiske testene er antall prøver, N. Her er kun et lite antall prøver målt og testet, og flere prøver burde bli målt for å oppnå et mer pålitelig resultat fra de statistiske testene. Dette er et viktig aspekt, og gjelder alle statistiske tester presentert i denne oppgaven.

Det er flere aspekter ved metoden som burde optimaliseres videre. Det viktigste er valg av yield monitor eller internstandard. ^{133}Ba ble brukt i dette prosjektet, hvor det ble antatt et likt tap av ^{133}Ba og ^{226}Ra. En test viste at forholdet mellom ^{226}Ra og ^{133}Ba forandret seg gjennom prosedyren – ^{226}Ra så ut til å ha en sterkere affinitet til kolonnematerialet. Forholdet forandret seg fra 33% til 43% gjennom prøveopparbeidelsen, og dette var for ferskvannsprøver. Det er derfor antatt at forholdet er enda mer forandret i mer komplekse matrikser. Korrigering med ^{133}Ba bør utføres med forsiktighet da forholdet mellom yield monitor/ISTD og analytt forandret seg gjennom prøveopparbeidelsen. Det påpekes at kun én test for ferskvann ble testet, så dette må testes videre. Å bruke en annen internstandard bør kanskje vurderes – Larivière et al. publiserte en artikkel i 2005 hvor ^{228}Ra ble brukt som yield monitor for jord- og sedimentprøver.

Slik metoden er presentert i denne oppgaven kan den brukes for bestemmelse av ^{226}Ra i vannprøver og jordprøver ved bruk av ICP-QQQ. Prosedyren ble ikke testet for biotaprøver, men det er ønskelig å få metoden opp for biotaprøver også. Derimot, resultatene er ikke fullt påliteligere på grunn av det endrende forholdet mellom ^{133}Ba og ^{226}Ra, mangel på parallelprøver og et lite antall prøver (N). Deteksjonsgrensen på 0,052 pg/L for vannprosedyre var under den øvre grensen satt av USEPA for deteksjonsgrenser ved analyse av drikkevann.

Contents

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Abbreviations

ANOVA	Analysis of Variance
ATSDR	Agency for Toxic Substances and Disease Registry
CEX	Cation Exchange
cpm	Counts per Minute
cps	Counts per Second
CRM	Certified Reference Material
DI-water	Deionized water
DPM	Disintegrations per Minute
EC	Electron Capture
EDTA	Ethylenediaminetetraacetic acid
EPA	United States Environmental Protection Agency
FW	Freshwater
Ge	Germanium detector
IC	Internal Conversion
ICP-QQQ-MS	Triple Quadrupole Inductively Coupled Plasma Mass Spectrometry
IEX	Ion Exchange
IUPAC	International Union of Pure and Applied Chemistry
LOD	Limit of Detection
LOQ	Limit of Quantification
LRM	Liquid Reference Material
LSC	Liquid Scintillation Counter
NaI	Sodium Iodine detector
NIST	National Institute of Standards and Technology
NMBU	Norwegian University of Life Science
NORM	Naturally Occurring Radioactive Material
NPRA	Norwegian Public Roads Administration
NRPA	Norwegian Radiation Protection Authority
PCA	Principal Component Analysis
PW	Produced Water
REE	Rare Earth Elements
TFM	3-Trifluoromethyl-4-nitrophenol
UC	UltraCLAVE
USEPA	United States Environmental Protection Agency
UW	UltraWAVE

1 Introduction

Four isotopes of radium exist naturally in the environment from the decay of uranium and thorium, and for the ^{238}U decay chain ^{226}Ra is the most important radionuclide (Park, Chang J. et al. 1998). The alpha emitter ^{226}Ra with a half-life of 1600 years, is considered a human carcinogen and a long-time exposure can lead to harmful effects such as anemia, fractured teeth, various types of cancer and death (ATSDR. 1999). Due to its radiological toxicity, the radium content in drinking water is strictly controlled in many countries. According to the public health statement of radium published by Agency for Toxic Substances and Disease Registry, the United States Environmental Protection Agency has set a limit of 5 pg Ra per liter drinking water. ^{226}Ra levels in groundwater vary over a wide range in Nordic countries if the wells are drilled in normal bedrock. The levels range from 0.3 to 6.8 pq/L (0.01 to 0.25 Bq/L), according to "*Natural Radioactivity in Produced Water from the Norwegian Oil and Gas industry in 2003"* published by Norwegian Radiation Protection Authority in 2005. The USEPA requires a detection limit lower than 1 pg ^{226}Ra/L (0.4 Bq/L) for the analytical method applied (Park, Chang J. et al. 1998).

A problem concerning the oil- and gas industry is produced water, which is water co-produced with oil and gas (NRPA. 2005). Produced water from Norwegian platforms may contain elevated levels of NORMs, Naturally Occurring Radioactive Materials, and especially the radium isotopes ^{226}Ra and ^{228}Ra. There are two factors affecting the release of NORMS from oil platforms – concentration of isotopes and the amount of produced water (NRPA. 2015). According to "*Natural Radioactivity in Produced Water from the Norwegian Oil and Gas industry in 2003"* published by NRPA in 2005, the activity concentrations of these radium isotopes are about three order of magnitude higher than the normal activity concentration found in seawater. The Troll platforms are located 60-80 kilometers outside Hordaland, and the production water from these platforms contains relatively high concentrations of radioactive matter (NRPA. 2015). The discharged activity of ^{226}Ra from platforms Troll B and Troll C corresponded to approximately 40 percent of the total discharged activity from the Norwegian continental shelf installations (NRPA, 2005). In 2012 approximately 437 GBq of ^{226}Ra was released from platforms located in the North Sea and the Norwegian Sea, and the released production water contained approximately 82 pg ^{226}Ra/L (3 Bq/L) (NRPA. 2015).

There are several methods that can be applied to determine the content of radium in water samples. These methods are based on different physical and chemical principles, and the methods differ in reachable detection limits, selectivity and reproducibility. The concentration of ^{226}Ra can be determined via the emitted alpha particle or gamma-ray emission. However, there are also methods where the concentration is determined indirectly via its progenies where radioactive equilibrium is required (Köhler et al. 2001). Köhler et al. published a study in 2001 where different methods for the analysis of ^{226}Ra in water samples were compared. The results of the study showed different duration of complete analysis, combined uncertainties, sensitivity and blank count rate – which are important parameters to consider when choosing a method to determine the concentration of ^{226}Ra in water samples.

Per August 2016, there are no methods in use at the Isotope Laboratory at NMBU Campus Ås, to determine the concentration of ^{226}Ra. Thus, the main goal for this master thesis is to develop an applicable method to determine the concentration of ^{226}Ra by triple quadrupole Inductively Coupled

Plasma Mass Spectrometry (ICP-QQQ), and compare the results with the results from measurement by Ge-detector to verify the results.

Köhler et al. concluded from their study that counting of alpha particles after $BaSO_4$-precitipation may not be the best method for ^{226}Ra-determination. The method reaches the required detection limits, but the duration of complete analysis, approximately 23 days, and being relatively analyst dependent, can exclude this method for the determination of ^{226}Ra (Köhler et al. 2001). The study published by Köhler et al. in 2001 did not include a measurement by ICP-MS, but the article mentions the growing possibility of measuring radionuclides with ICP-MS. Kim et al. published a study in 1999 where the content of ^{226}Ra in groundwater was determined by High Resolution ICP-MS without coprecipitation with $BaSO_4$, and the procedure used in this study has been taken into account when developing a method for measuring ^{226}Ra in environmental samples at the Isotope Laboratory, Campus Ås.

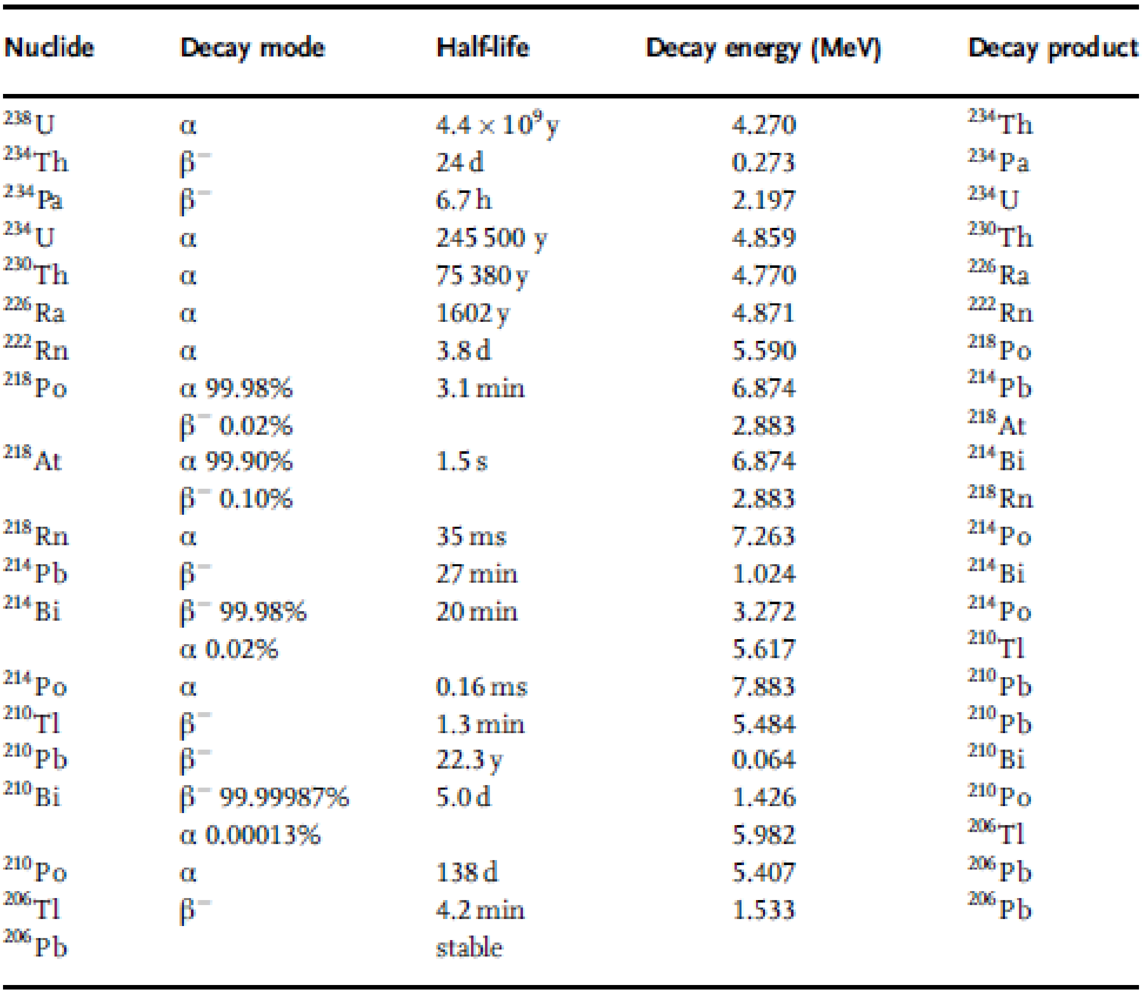
The goal is to develop a procedure, which can be applied to various types of environmental samples with different types of matrices, e.g. freshwater, produced water and soil. The goal for the procedure is to avoid coprecipitation with $BaSO_4$ and fewer matrices, and being less time-consuming procedure if there is an urgent need for results. The speciation of ^{226}Ra, which means different forms of radium, has not been taken into account when the focus is quantifying the amount of ^{226}Ra.

2 Theoretical Background: Radiation and Radium-226

2.1 Natural Radionuclides and Types of Radiation

Radioactive radiation is radiation that is emitted from the core of a radionuclide, and a radionuclide is a radioactive form of an element. There are found three types of radionuclides in the nature: radionuclides from the decay chains of uranium and thorium, single very long-lived radionuclides, and cosmogenic radionuclides (Hou, X. and Letho, J. 2012). The radionuclides from the decay chain of uranium and thorium will be discussed further.

The decay chain of uranium and thorium starts with ^{235}U, ^{238}U and ^{238}Th, and these isotopes were formed at the beginning of the Universe around 13,7 billion years ago. The decay chains end with stable isotopes of lead, ^{207}Pb, ^{206}Pb and ^{208}Pb. 42 radionuclides of 13 isotopes are in between the start and finish of these decay chains. Figure 1 show the decay chain for ^{238}U, where the trace element of interest in this thesis, ^{226}Ra, is found (Hou, X. and Letho, J. 2012).



Nuclide	Decay mode	Half-life	Decay energy (MeV)	Decay product
^{238}U	α	4.4×10^9 y	4.270	^{234}Th
^{234}Th	β⁻	24 d	0.273	^{234}Pa
^{234}Pa	β⁻	6.7 h	2.197	^{234}U
^{234}U	α	245 500 y	4.859	^{230}Th
^{230}Th	α	75 380 y	4.770	^{226}Ra
^{226}Ra	α	1602 y	4.871	^{222}Rn
^{222}Rn	α	3.8 d	5.590	^{218}Po
^{218}Po	α 99.98%	3.1 min	6.874	^{214}Pb
	β⁻ 0.02%		2.883	^{218}At
^{218}At	α 99.90%	1.5 s	6.874	^{214}Bi
	β⁻ 0.10%		2.883	^{218}Rn
^{218}Rn	α	35 ms	7.263	^{214}Po
^{214}Pb	β⁻	27 min	1.024	^{214}Bi
^{214}Bi	β⁻ 99.98%	20 min	3.272	^{214}Po
	α 0.02%		5.617	^{210}Tl
^{214}Po	α	0.16 ms	7.883	^{210}Pb
^{210}Tl	β⁻	1.3 min	5.484	^{210}Pb
^{210}Pb	β⁻	22.3 y	0.064	^{210}Bi
^{210}Bi	β⁻ 99.99987%	5.0 d	1.426	^{210}Po
	α 0.00013%		5.982	^{206}Tl
^{210}Po	α	138 d	5.407	^{206}Pb
^{206}Tl	β⁻	4.2 min	1.533	^{206}Pb
^{206}Pb		stable		

Figure 1. Uranium Decay Chain. (Hou, X. and Letho, J. 2012).

A radionuclide has an unstable nucleus, which indicates that it is radioactive. The instability within the nuclei comes from an inappropriate neutron to proton-ratio, or the mass of the nucleus is too high. The unstable nucleus will emit radioactive radiation to adjust the neutron to proton-ratio, or dispose the excess mass to achieve the requirements for a stable nucleus (Hou, X. and Letho, J. 2012).

2.1.1 Types of Radiation

There are four different types of radioactive modes an unstable nucleus can undergo: fission, alpha-decay, beta-decay and internal conversion. Fission is the characteristic radioactive mode for the heaviest elements, but will not be discussed any further in this thesis. The main focus will be on alpha radiation, since ^{226}Ra is an alpha emitter. ^{226}Ra is the radionuclide of interest in this thesis, and will be used as an example when explaining alpha radiation. Since the radium-isotopes have different decay, beta radiation and internal transition will be introduced briefly as well.

In addition to fission, alpha radiation is also a typical decay mode for heavy radionuclides. The heavy radionuclides have an excess of mass, and during alpha radiation, the heavy nucleus emits a helium nucleus to get rid of the excess mass. The helium nucleus is called an alpha particle, α (Hou, X. and Letho, J. 2012). This is shown in equation 1:

$$^{226}_{88}\mathrm{Ra} \rightarrow \ ^{222}_{86}\mathrm{Rn} + \ ^{4}_{2}\mathrm{He} \tag{1}$$

When ^{226}Ra emits an alpha particle, it will decay into ^{222}Rn. The mass number decreases by four units and the atomic number decreases by two units, as shown in equation 1. This applies for all radionuclides with an alpha decay mode. The energy of an alpha particle is typically between 4-7 MeV (Hou, X. and Letho, J. 2012). The transformation from mother nuclide to daughter nuclide will take place in defined energy levels, thus the emitted alpha particle will always have the same energy for the specific radionuclides. The energy of the alpha particle emitted by ^{226}Ra is 4.785 keV according to the Live Chart of Nuclides April 2014.

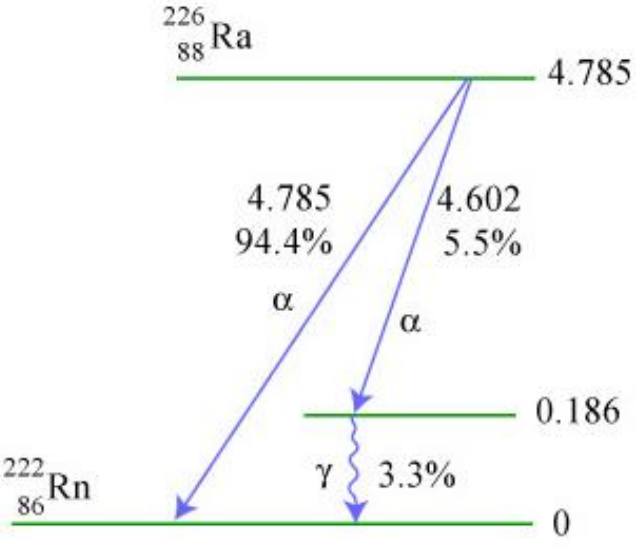


Figure 2. Nuclear Decay Scheme of ^{226}Ra. (MIT OpenCourseWare, 2007)

Figure 2 shows the decay process for ^{226}Ra, and it shows that the decay does not only lead to the ground state of ^{222}Rn, but to an excited energy state as well. The fractions of decay processes are called intensities, and they have certain probabilities. 95% of the decay processes directly lead to the daughter in ground state, whereas 5.5% lead to an excited state of the daughter nuclide. As seen in figure 2, the alpha particle leading to this excited state has a lower energy, 4.6 MeV compared to 4.8 MeV. As mentioned earlier the same amount of energy should be released in each decay process, and excited states also represent defined quantum states. Hence, the energy difference between the excited state and ground state is emitted as electromagnetic gamma radiation or as conversion electrons.

Gamma emissions are often easier to measure than alpha particles, so if the energies of the gammas are high enough it is advantageous to measure the activity of the mother nuclide by the gamma emissions. ^{226}Ra does not have a detectable gamma emission, since the intensity of the gamma energies are not high enough.

Beta radiation is characteristic for the lighter radionuclides, and these elements do not have the required neutron to proton ratio for stability – the ratio is either too high or too low. To reach this required stability ratio the element converts a proton to a neutron or vice versa, as shown in equation 2 and 3.

$$\text{Neutron} \rightarrow \text{Proton} + e^- \ (\beta^-) \tag{2}$$

$$\text{Proton} \rightarrow \text{Neutron} + e+ \ (\beta+) \tag{3}$$

Equation 2 represents beta minus decay. This process takes place when the nucleus has too many neutrons, and will transform a neutron into a proton. Hence, the mass number is the same for the daughter as for the mother, but the atomic number will increase by one unit. The electromagnetic charge has to be preserved, so the mother will emit a beta minus particle. The beta minus particle (β^-) is equal to an electron physically; same mass and a charge at -1. ^{228}Ra is another isotope of radium, is a daughter of ^{232}Th. ^{228}Ra is a pure beta minus emitter. Equation 3 represents beta plus decay, which takes place when the nucleus is proton rich – too many protons. The nucleus will transform a proton into a neutron, and emit a positron from the core (β+). A positron is an antiparticle of an electron. It has the same mass, but a charge of +1 (Hou, X. and Letho, J. 2012).

The collective term for gamma emission or internal conversion (IC) is internal transition, and is the final type of decay mode explained in this section. As mentioned earlier when a radionuclide decay by alpha or beta radiation, it often goes through excited states of the daughter. The excited daughter nuclide emits gamma radiation or undergoes internal conversion to return to the ground state. Also mentioned earlier, these excited states have defined quantum levels, and therefore these gamma rays are monoenergetic. The spectrum obtained from these gamma rays make a peak spectrum (Hou, X. and Letho, J. 2012). Gamma radiation is an electromagnetic radiation, where photons are emitted from the core of the radioactive nuclides, whereas alpha- and beta radiation are particles.

IC is a competitive process with gamma emission, and during IC excitation energy is transferred to an electron in an atomic electron shell of the daughter nuclide. This energy transfer is the difference between the de-excitation energy and the binding energy of the electron; hence, these electrons are monoenergetic. The electron hole can be filled with an electron from one of the upper shells, which will create X-rays and Auger electrons (Hou, X. and Letho, J. 2012).

The energies for α, β, or γ-radiation are characteristic for the radiation emitting nuclide, and therefore this is the qualitative measure of radiation. The quantitative measure is the intensity of the radiation.

2.2 Radium-226 as an element

2.2.1 Alkaline Earth Metals – Chemical Properties

The most important alkaline earth metals with radioactive properties in an environmental aspect are ^{90}Sr, ^{226}Ra and ^{228}Ra. ^{226}Ra and ^{228}Ra-isotopes are generated in the natural radioactive decay series, as mentioned in chapter *1.1 Natural Radionuclides and Types of Radiation*, and they are respectively alpha- and beta emitters.

The alkaline earth metals belong in group two in the periodic table, which means they have 2s-orbital electrons in their outer shell. The alkaline earth metals form compounds in oxidation state +II, and will appear as M^{2+}ions in aqueous solutions. The alkaline earth metals are less electropositive than the alkali metals, due to smaller size. Both ^{226}Ra and ^{228}Ra are the most electropositive of the alkaline earth metals, since the electropositivity increases with atomic number. Due to this electropositive property, the alkaline earth metals form ionic bonds, and their common compounds are highly soluble (Hou, X. and Letho, J. 2012).

2.2.2 Radium-226

Naturally there exist four isotopes of radium, formed in the decay of uranium and thorium, as mentioned in chapter *1.1 Natural Radionuclides and Types of Radiation* (Hou, X. and Letho, J. 2012). For ^{238}U decay chain, the most important radionuclide is ^{226}Ra with a half-life of 1600 years. According to United States Environmental Protection Agency "*every radionuclide emits radiation at its own specific rate, which is measured in terms of half-life*" (EPA. 2015). ^{226}Ra is formed from the alpha decay of ^{230}Th, and ^{226}Ra will decay further into ^{222}Rn, as shown in figure 1. As mentioned earlier, there are gamma rays emitted when ^{226}Ra decays into ^{222}Rn, but the intensity (5.6%) is so low that the gamma radiation cannot be used for direct measurement of ^{226}Ra in low activity samples (Hou, X. and Letho, J. 2012). Figure 2 shows that the energy of the strongest gamma transition is at 186 keV, which is the same as for the almost equally intense peak for ^{235}U. Therefore, ^{226}Ra is usually determined by measuring the alpha radiation or indirectly measuring the alpha radiation of its progeny by LSC.

3 Materials and Methods

The goal for this master project was to develop an applicable method to determine the content of ^{226}Ra in environmental samples using ICP-MS triple quadrupole. The focus of this chapter will be on the development of the procedure, and will be divided into two main parts – sample preparation, and optimization and measurement of ^{226}Ra in unknown environmental samples. The two parts will again be divided into subchapters.

Various types of environmental samples were prepared by the procedure presented in this chapter. The samples had different matrices, and the environmental samples included freshwater, produced water, and soil samples. By testing different types of samples, it was possible to check if the method was applicable to various types of matrices – which is desirable.

The produced water-samples from Troll C are a part of the master project *"Changes in Speciation and Kinetics of Po-210 in Produced Water from Oil Industry when mixed with Seawater"* by Mekhonina, V. The produced water samples were from the Norwegian oil platform Troll C, the salinity of produced water are about 4.8% (w/V) compared to 3.0-3.5% (w/V) in seawater (Mekhonina, V. 2017). The four produced water samples were fractionated: Blank (seawater), <10 kDa, <0.45 μm and Total (Mekhonina, V. 2017). Mekhonina, V. performed the fractionation.

The formation water-samples were given by the Central Mining Institute of Silesian Centre for Environmental Radioactivity. The water is formation water with radium isotopes, both ^{226}Ra and ^{228}Ra, and the formation water has been measured several times by many laboratories. Thus, it is considered as a Liquid Reference Material (LRM), bottle 99 and 103 were used in this thesis. The total volume of each bottle was two liters. The preparation of the formation water, performed by the Central Mining Institute in Poland, can be found in the evaluation report from 2016 called "*Radium Isotopes in Water – Interlaboratory Comparison (ILC). Evaluation Report*" written by Bonczyk, M. and Michalik, B. (Bonczyk, M., Michalik, B. 2016).

The freshwater samples and soil samples from Orrefjell are a part of the Orrefjell-project "Case Orrefjell". The freshwater- and soil samples were sampled by NRPA from Orrefjell, station 2, located in Troms in Norway, and it is known that there is high abundance of uranium in this area – thus, it is expected to high abundance of ^{226}Ra as well (Scandinavian Highlands Holding A/S. 2016). GPS-coordinates for the sampling station can be found in table *E3*, attachment *6.2 Soil Samples*. The other soil samples are a part of the master project "*Uranium and Toxic Metal Uptake by the Earthworm Eisenia Hortensis in Contaminated Soils*" by Schöpke C.. Preparation of the soil samples prior to the preparation according to the procedure presented in this thesis, was performed by Schöpke, C. (Schöpke, C. 2017). The results for these soil samples from the new method are compared with the Ge-measurement performed by NRPA Tromsø (Mauring, A. 2015).

The alum shale-sample was given to this master project, and the sample batch were a part of Norwegian Public Roads Administration's (NPRA) project 603019, called "*Construction works in areas with sulphide containing rock – case: effects and environmental risks related to alum shale disposal site"* from 2016 (Skipperud et al. 2016).

3.1 Sample Preparation – Cation Exchange

A study published by Kim et al. in 1999, determined ^{226}Ra in groundwater and soil by using high-resolution inductively coupled plasma-mass spectrometry (HR-ICP-MS), called "*Determination of ^{226}Ra in Environmental Samples using High-Resolution Inductively Coupled Plasma Mass Spectrometry*". The new procedure for quantifying the activity of ^{226}Ra in environmental samples in this thesis has taken the article and study by Kim et al. from 1999 into account and optimized for the optimal use in the Isotope Laboratory, NMBU Ås.

3.1.1 Materials for Developed Method – Water and Soil

A stock solution of 9.30 ng ^{133}Ba/L (88.0 Bq ^{133}Ba/mL) was used as a yield monitor/ISTD for water samples, and was prepared by diluting 0.5 mL ^{133}Ba from a stock solution 0.12 mg/L (4.50 kBq/mL), 2.5 mL 12M HCl and DI-water to a total volume of 50.0 mL in Sartedt centrifuge tubes.

A second stock solution of 18.4 ng ^{133}Ba/L (176 Bq ^{133}Ba/mL) was used as a yield monitor/ISTD for soil samples, and was prepared by diluting 1.0 mL ^{133}Ba from a stock solution 0.12 mg/L (4.50 kBq/mL), 2.5 mL 12M HCl and DI-water to a total volume of 50.0 mL in Sartedt centrifuge tubes.

A stock solution of approximately 10.0 ng ^{226}Ra /L (365 Bq ^{226}Ra/mL) was prepared by dilution of an accurately weighed amount of the standard solution of ^{226}Ra with 1% (V/V) nitric acid and DI-water, to a total volume of 50.0 mL. The stock solution was diluted to appropriate concentrations for making the calibration curve, as shown below:

	Calibration blank	Standard 1	Standard 2	Standard 3	Standard 4
^{226}Ra Standard ng/L	0.0000	0.0200	0.100	0.500	2.00
^{226}Ra Standard Bq/L	0.0000	0.730	3.65	18.3	73.0

The preparations of the solvents used in the procedure can be found in attachment *2.1 Preparations of Diluted Acids, EDTA and Ammonium Acetate – Ion Exchange.* Examples of the calculations are also presented in this attachment.

Aluminum Standard for ICP: Sigma-Aldrich, product number 61935. 1000 mg/L Al in HNO_3, Grade: TraceCERT. 1000 mg/L Al in 2% HNO_3, prepared with high purity $Al(NO_3)3*9H_2O$, HNO_3 and water. Certified in accordance with ISO/IEC 17025 and ISO Guide 34.

Analytical grade reagents

Bio-Rad AG 50W-X12: 500 g, Analytical Grade Cation Exchange Resin, hydrogen form, 12% cross linkage, 100–200 dry mesh size, 106–250 µm wet bead size, ~400 MW limit

Bio-Rad Glass Econo-column (10 cm*1 cm) with a porous polymer bed support at the bottom of the column. Econo-Column Chromatography columns from Bio-Rad are high-quality, low-pressure, glass chromatography columns.

Gilson MINIPLUS 3 Peristaltic Pump, 4 channels.

High purity deionized water

Hose: Reference 070534-08/ENE08-SC0008. Formulation TYGON R3607. ID: 0.76 mm Wall: 0.86 mm. Color code: black/black. LOT 737147

ICP-MS Complete Standards – IV – ICPMS-71A-125 mL: Inorganic Ventures. Certified in accordance with ISO/IEC 17025 and ISO Guide 34. Matrix HNO_3. Traceable to NIST. Elements: Al, As, Ba, Be, B, Cd, Ca, Ce, Cs, Cr^{3+}, Co, Cu, Dy, Er, Eu, Gd, Ga, Ho, Fe, La, Pb, Lu, Mg, Mn, K, Pr, Rb, Sm, Se , Ag, Tl, Th, Tm, U, V, Yb and Zn

ICP-MS Refractory Elements Standard – IV – ICPMS-71B-125 mL: Inorganic Ventures. Certified in accordance with ISO/IEC 17025 and ISO Guide 34. Matrix HNO_3/HF. Traceable to NIST. Elements: Sb, Ge, Hf, Mo, Nb, Si, Ta, Te, Sn, Ti, W and Zr

ICP-MS Refractory Elements Standard – IV – ICPMS-71D-125 mL: Inorganic Ventures. Certified in accordance with ISO 17025 and ISO Guide 34. Matrix HNO_3. Traceable to NIST. Elements: Li^{6+}, Bi, In, Sc, Tb and Y.

Inductively Coupled Plasma Mass Spectrometer: 8800 QQQ ICP-MS Agilent Technologies

Iron Standard for ICP: Sigma-Aldrich, product number 43149. 1000 mg/L Fe in HNO_3, Grade: TraceCERT. 1000 mg/L Fe in 2% HNO_3, prepared with high purity Fe metal, HNO_3 and water. Certified in accordance with ISO/IEC 17025 and ISO Guide 34.

Retsch Mortar Grinder RM 200

Sartedt 50.0 mL centrifuge tubes

Sodium Iodine Detector: 1480, RiaCalc WIZ, program 3,6 serial #4800419

UltraCLAVE IV from Milestone Inc.: 6 individual sample containers made of TFM

UltraWAVE from Milestone Inc.: 15 individual sample containers of TFM

3.1.2 Procedure of Water Samples

Before measuring any samples containing radioactivity, the whole procedure was tested with DI-water to optimize the procedure for the use in the Isotope Laboratory. The tests done in this part of the development stage, included sample- and cation resin load onto glass column according to the procedure in the article published by Kim et al. in 1999, but also leaching and duration of full analysis.

When using ion exchange-chromatography the sample needs to be in a liquid state. This meant that the water samples did not need any sample preparation prior to ion exchange-separation, whereas the soil samples needed to be digested into liquid state. The development of optimal digestion of soil samples and the full procedure for soil samples are presented in chapter *3.1.5 Acid Digestion and Sample Preparation of Soil Samples*. The following procedure represents the procedure for water samples:

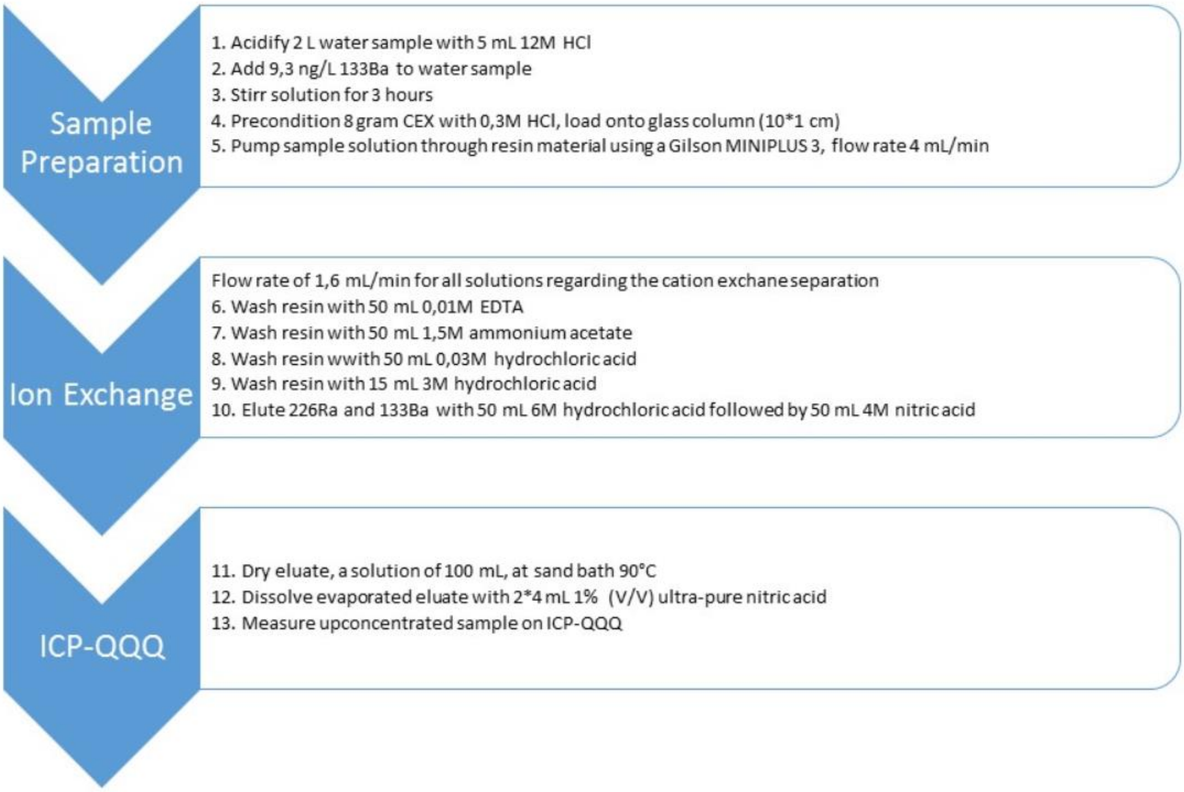
Two liter of water sample was acidified with 5 mL concentrated hydrochloric acid (pH 2), before 1 mL 9.30 ng/L ^{133}Ba (88.0 Bq/mL) was added to the water solution as a radiochemical yield monitor and internal standard. The solution was stirred for three hours using a magnetic stirrer.

8 grams of cation exchange resin (Bio-Rad AG 50W-X12) was weighed out and preconditioned with approximately 10 mL 0.3M hydrochloric acid before loaded onto a glass column (10 cm*1 cm). After the acidified two liter water sample, pH 2.5, had stirred for three hours, it was passed through the cation exchange column using a Gilson MINIPLUS 3 peristaltic pump with a flow rate of approximately 4 mL/min, and collected into a new glass beaker.

All the solutions in the following ion exchange steps were passed through the column using the Gilson MINIPLUS 3 Peristaltic pump with a flow rate of 1.6 mL/min. The resin was washed with 50 mL 0.01M EDTA, Ethylenediaminetetraacetic acid, solution. 50 mL of 1.5M ammonium acetate was added for elimination of matrices like Ca, Mg and Sr. The resin was washed gradually with 50 mL of 0.03M hydrochloric acid. The EDTA-solution and the ammonium acetate was cleaned out with 15 mL 3M hydrochloric acid. ^{226}Ra and ^{133}Ba was eluted with 6M 50 mL hydrochloric acid followed by 50 mL 4M nitric acid.

The eluate containing both ^{226}Ra and ^{133}Ba, was evaporated to dryness for further up concentration at a sand bath, 90˚C. The evaporated eluate was dissolved with 2*4 mL 1% (V/V) ultra-pure nitric acid. The chemical recovery, ^{133}Ba, was measured by a NaI-detector for 10 minutes. The solution was then injected into an ICP-QQQ, and the recovery of ^{133}Ba as internal standard and ^{226}Ra was counted.

Figure 3 shows an illustration of the method for water samples.



1. Acidify 2 L water sample with 5 mL 12M HCl
2. Add 9,3 ng/L 133Ba to water sample
3. Stirr solution for 3 hours
4. Precondition 8 gram CEX with 0,3M HCl, load onto glass column (10*1 cm)
5. Pump sample solution through resin material using a Gilson MINIPLUS 3, flow rate 4 mL/min

Flow rate of 1,6 mL/min for all solutions regarding the cation exchane separation

6. Wash resin with 50 mL 0,01M EDTA
7. Wash resin with 50 mL 1,5M ammonium acetate
8. Wash resin wwith 50 mL 0,03M hydrochloric acid
9. Wash resin with 15 mL 3M hydrochloric acid
10. Elute 226Ra and 133Ba with 50 mL 6M hydrochloric acid followed by 50 mL 4M nitric acid

11. Dry eluate, a solution of 100 mL, at sand bath 90°C
12. Dissolve evaporated eluate with 2*4 mL 1% (V/V) ultra-pure nitric acid
13. Measure upconcentrated sample on ICP-QQQ

Figure 3. Schematic overview over procedure for water samples.

3.1.3 Spiked Water Samples

Before any real samples containing ^{226}Ra, were prepared by the procedure presented in the previous chapter, spiked samples containing known amounts of ^{226}Ra were prepared. Different known concentrations of ^{226}Ra, and yield monitor/ISTD ^{133}Ba, were added to deionized water (DI-water). The samples were prepared by the procedure presented in *3.1.2 Procedure of Water Samples*. A stock solution of approximately 547 pg ^{226}Ra/L (20.0 Bq/L) was used to prepare spiked samples with different concentrations of ^{226}Ra. The concentration range for ^{226}Ra in the spiked samples is presented in table 1:

Table 1. Concentrations of ^{226}Ra in pg/L and Bq/L in spiked samples.

	Blank	Sample 1	Sample 2	Sample 3	Sample 4
pg ^{226}Ra/L	0.0000	$2.73*10^{-3}$	0.027	0.27	2.7
Bq ^{226}Ra/L	0.0000	0.0001	0.001	0.01	0.1
ng/L ^{133}Ba		9.30	9.30	9.30	9.30

The calculations for preparing the stock solutions, spiked samples and external standards can be found in attachment *2.3 Preparation of ^{226}Ra Stock Solutions*, and *2.4 Preparation of ^{226}Ra Standards – Calibration Curve*.

3.1.4 Recovery of ^{133}Ba in Different Matrices

As a part of the sample preparation, the recovery of ^{133}Ba, and thus, ^{226}Ra, was measured on NaI-detector. The recovery of ^{133}Ba was measured after each step, as presented below, of the procedures presented in chapter *3.1.2 Preparation of Water Samples* and *3.1.6 Procedure of Soil Samples*. The solutions after each step was measured to determine critical steps of the procedure. A reference solution was prepared by adding 1 mL 9.30 ng/L ^{133}Ba to 8 mL DI-water, and measured on NaI simultaneously as the solutions presented below. A recovery test was also performed with DI-water and 1 mL 9.30 ng/L ^{133}Ba as yield monitor to determine the optimal flow rate of acid solutions in the ion exchange-separation. A sample illustrating produced water was also prepared; DI-water, 1 mL 9.30 ng/L ^{133}Ba with 4.8 % (w/V) NaCl (Mekonina, V. 2017).

The sequence of solutions measured on NaI-detector for detection of loss and recovery of ^{133}Ba, were as following:

Ion Exchange				**Sample Solution**	**Reference; 1 mL 9.30 ng/L ^{133}Ba**	**Water passed through column**	
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
20 mL 0.01M EDTA	20 mL 1.5M $C_2H_7NO_2$	20 mL 0.03M HCl	15 mL 3M HCl	2*4 mL sample, 1% HNO_3	8 mL ^{133}Ba reference	20 mL “waste water”	Column material

The recovery tests described above, the solutions (1-8) were measured on NaI for all prepared samples presented in this thesis. This was performed to determine the recovery and loss of ^{133}Ba and analyte in different matrices.

3.1.5 Acid Digestion and Sample Preparation of Soil Samples

As mentioned, the soil samples needed to be digested before ion exchange-separation. Barium, and radium, will be almost insoluble when bound as sulphates digested with HNO_3 HCl and HF. Thus, the focus on this section was to find the optimal digestion of barium.

When investigating which acid solution would be preferred for digestion of soil samples containing barium and radium, two certified reference materials were used; NCS ZC73007 and NIST 2709a. Two parallels of each CRM of approximately 0.2g were weighed into UltraWAVE-vials made of TFM. The parallels were added either 2 mL HNO_3, 1 mL HF and 3 mL HCl or 2 mL HNO_3 and 3 mL HCl. The samples were digested at 260˚C for 40 minutes in an UltraWAVE (UW), 15 positions. It was determined prior to the experiment that the acid-solution with the most accurate result, in other words best recovery of barium, would be used for digestion of soil samples unless poor recovery-results were obtained.

For further testing of the optimal digestion technique for barium, and radium, several certified reference materials, CRM, were used to make sure the method was applicable to several types of mineral bound barium. The following certified reference materials were used:

CRM		**Matrix**	**Certified Value of Ba, (mg/kg)**
GBW07401	Institute of Geophysical And Geochemical Exploration	Soil	590 ± 15
GBW07403	Institute of Geophysical And Geochemical Exploration	Soil	1210 ± 30
NIST 2710a	National Institute of Standards and Technology	Soil	792 ± 36
NIST 2711a	National Institute of Standards and Technology	Soil	730 ± 15
NCS DC 73325	China National Analysis Center for Iron & Steel 2003	Soil	180 ± 27
NCS ZC 73007	China National Analysis Center for Iron & Steel 2003	Soil	411 ± 18
NIST 2709a	National Institute of Standards and Technology	Soil	979 ± 28

Two parallels of each CRM of approximately 0.2 g were prepared in UW-vials. The parallels were added either 4 mL H_3PO_4, 2 mL HNO_3, and 2 mL HBF_4 or 4 mL H_3PO_4 and 2 mL HNO_3. The samples were all digested by UW at 260˚C for 40 minutes, and transferred into 50 mL-Sartedt centrifuge tubes. The samples were diluted to 50 mL with DI-water. Before measurement on ICP-MS with O_2 as reaction gas, the samples were diluted 100 times – 150 µL sample solution, 0.75 mL ultra-pure HNO_3, 150 µL internal standard (200 µg Rh/L) diluted with DI-water to a total volume of 15 mL. Three blank samples were also prepared with 4 mL H_3PO_4, 2 mL HNO_3, and 2 mL HBF_4.

Standards used for determination of Ba in CRM on ICP-MS can be found in attachment *4 Digestion of Soil Samples*, table *C1*.

3.1.6 Sample Preparation of Soil Samples

The full procedure for soil samples were as following, and is presented in figure 4:

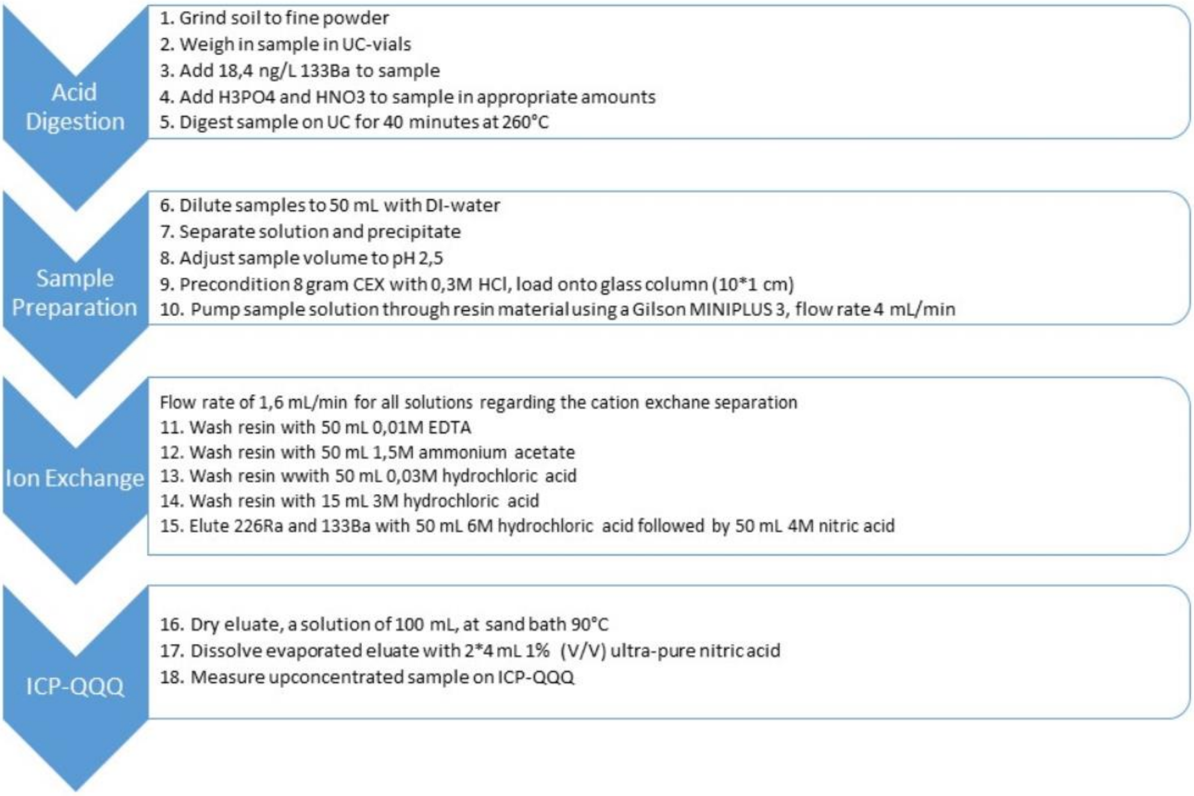
Prior to digestion on UltraCLAVE (UC), the soil samples were ground to fine powder using a Retsch Mortar Grinder RM 200. The samples were grounded separately for 4 minutes to mix and homogenize the soil – thus, increasing the surface area allowing the process to proceed more rapidly. 5 grams of soil were weighed in directly in UC-vials (PTFE-vials, 6 positions), and added 25 mL of H_3PO_4 and 1 mL 18.4 ng/L ^{133}Ba (176 Bq/mL) as a radiochemical yield monitor and internal standard. The amount of HNO_3 in mL used depended on the content of organic matter present in the soil – it varied from 12-20 mL. The amount of H_3PO_4 remained constant for all soil samples digested.

The samples were digested by UC at 260˚C for 40 minutes and diluted to 50 mL before sedimentation. The samples were filtrated through a Whatman Blue Ribbon-filter, Ø 110 mm, to separate precipitation and solution. After filtration the samples were diluted to approximately 2 liters: pH 2.5.

8 grams of cation exchange resin (Bio-Rad AG 50W-X12) was preconditioned with approximately 10 mL 0.3M hydrochloric acid, and loaded onto a Bio-Rad Glass Econo-column (10 cm*1 cm). The soil sample-solution was pumped through the column using a Gilson MINIPLUS 3 peristaltic pump with a flow rate of 4 mL/min. The solution, which has passed through the column, was collected into a new glass beaker – waste.

The following steps were part of the ion exchange separation. The solutions were pumped through the column with a flow rate of 1.6 mL/min, using Gilson MINIPLUS 3 peristaltic pump. First, the column was washed with 50 mL 0.01M EDTA, Ethylenediaminetetraacetic acid, solution. The column was then washed with 50 mL 1.5M $C_2H_7NO_2$, Ammonium acetate, for elimination of matrix elements like Ca, Mg and Sr. The column was then washed with 0.03M hydrochloric acid, following a wash with 15 mL 3M hydrochloric acid to wash out the EDTA-solution and the ammonium acetate. 6M hydrochloric acid followed by 50 mL 4M nitric acid were used to elute ^{226}Ra and ^{133}Ba with 50 mL, and the eluate was collected in the same beaker – total volume of 100 mL.

The eluate, which contains both ^{226}Ra and ^{133}Ba, was evaporated to dryness in a sand bath, 90˚C. The evaporated eluate was dissolved in 2*4 mL 1% ultra-pure nitric acid. The chemical recovery of ^{133}Ba was measured on NaI-detector. The up concentrated sample was injected into an ICP-QQQ, and the chemical recovery of ^{133}Ba as internal standard and content of ^{226}Ra was measured.



1. Grind soil to fine powder
2. Weigh in sample in UC-vials
3. Add 18,4 ng/L 133Ba to sample
4. Add H3PO4 and HNO3 to sample in appropriate amounts
5. Digest sample on UC for 40 minutes at 260°C

6. Dilute samples to 50 mL with DI-water
7. Separate solution and precipitate
8. Adjust sample volume to pH 2,5
9. Precondition 8 gram CEX with 0,3M HCl, load onto glass column (10*1 cm)
10. Pump sample solution through resin material using a Gilson MINIPLUS 3, flow rate 4 mL/min

Flow rate of 1,6 mL/min for all solutions regarding the cation exchane separation

11. Wash resin with 50 mL 0,01M EDTA
12. Wash resin with 50 mL 1,5M ammonium acetate
13. Wash resin wwith 50 mL 0,03M hydrochloric acid
14. Wash resin with 15 mL 3M hydrochloric acid
15. Elute 226Ra and 133Ba with 50 mL 6M hydrochloric acid followed by 50 mL 4M nitric acid

16. Dry eluate, a solution of 100 mL, at sand bath 90°C
17. Dissolve evaporated eluate with 2*4 mL 1% (V/V) ultra-pure nitric acid
18. Measure upconcentrated sample on ICP-QQQ

Figure 4. Schematic overview over procedure for soil samples.

3.1.7 ^{133}Ba as Yield Monitor and Internal Standard

^{133}Ba was, as mentioned previously, used as a yield monitor and ISTD for ^{226}Ra. It was assumed that the two isotopes had similar chemical behavior – the loss of ^{226}Ra was assumed equal to the loss of ^{133}Ba. A test to check this assumption was performed. By adding known concentration of both ^{133}Ba and ^{226}Ra to a sample, it was possible to determine whether or not ^{133}Ba was a good yield monitor or internal standard for ^{226}Ra.

9.30 ng ^{133}Ba (88.0 Bq) and 1.4 ng ^{226}Ra (0.05 Bq) were added to two liter DI-water, and was prepared by the procedure presented in chapter *3.1.2 Procedure of Water Samples*. A reference-solution was also prepared by diluting 9.30 ng/L ^{133}Ba (88.0 Bq/mL) and 1.4 ng/L ^{226}Ra (0.05 Bq/L) to a total volume of 8 mL with DI-water. This reference-solution was measured directly on ICP-QQQ after preparation, whereas the test-sample was measured after ion exchange-separation. The ratio between ^{226}Ra /^{133}Ba in test-sample and ratio between ^{226}Ra /^{133}Ba in reference solution was compared. If the ratios were similar or equal, ^{133}Ba would be considered a good yield monitor and internal standard for ^{226}Ra. A simple figure is displayed below in figure 5 on how this experiment was set up.

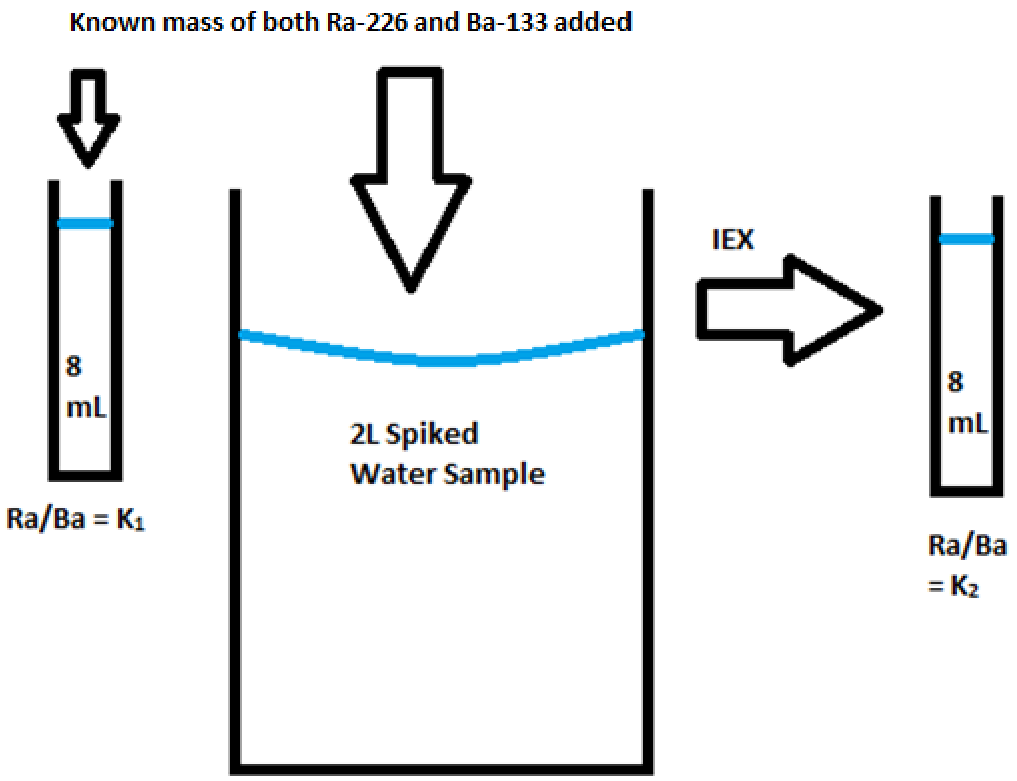


Figure 5. Simple illustration of test performed for testing ^{133}Ba as yield and ISTD.

3.2 Determination of ^{226}Ra in Unknown Environmental Samples

This chapter focuses on optimizing the instrument parameters and measurement of ^{226}Ra in unknown environmental samples.

3.2.1 Optimization of the Instrument – Interferences

Prior to measurement of samples containing ^{226}Ra, the instrument was optimized. Two different gas-modes were tested to optimize the measurements on ICP-QQQ: no gas and nitrous oxide. The flow of N_2O was optimized to obtain a good as possible signal from RaO^+ and BaO^+, and to minimize the signals from the interfering polyatomic masses (signal-to-noise).

Prior to measurement of samples containing ^{226}Ra, solutions containing lead, tungsten, fluoride and cesium, respectively Pb, W, F and Cs, were measured to test the optimal gas mode and instrument parameters to minimize the influence of the polyatomic interferences. The solutions had the following concentrations:

	Pb**	**W**	**Cs**	**71ABD***
Concentration, µg/L	20	20	20	20

*0.2% Fluoride

** 1.0 mg/L Ca

3.2.2 Standards and Standard Curve

To quantify ^{226}Ra in unknown environmental samples using ICP-QQQ, a multiple-point standardization was applied using external standards with internal standard. The standards were prepared for both water samples and soil samples. The external standards were prepared by diluting the stock solution, 10.0 ng ^{226}Ra/L (366 Bq/L), to the appropriate concentrations. The concentration range for ^{226}Ra in the external standards is found in table 2:

Table 2. Concentrations of ^{226}Ra in external standards used for determination of ^{226}Ra in unknown environmental samples. Significant figures: 3.

	Calibration blank	Standard 1	Standard 2	Standard 3	Standard 4
ng ^{226}Ra/L	0.0000	0.0200	0.100	0.500	2.00
Bq ^{226}Ra/L	0.0000	0.730	3.65	18.3	73.0

The calculations for preparing the external standards can be found in attachment *2.4 Preparation of ^{226}Ra Standards – Calibration Curve*. All standards were added 6.25 mL ^{133}Ba as internal standard to illustrate the upconcentrated amounts of ^{133}Ba and 0.5 mL ultra-pure HNO_3.

By measuring the signal of ^{226}Ra on ICP-QQQ, and plotting it against the known concentrations of the analyte an external standard curve was made. The standards were measured in gas mode "N_2O" with both S-lens and X-lens, and the instrument parameters of ICP-QQQ can be found in attachment *1.1 Inductively Coupled Plasma Mass Spectrometry*.

3.2.3 Water samples

There are several water samples used for determination of ^{226}Ra by ICP-QQQ, both freshwater, produced water and formation water. The freshwater samples were collected by NRPA Tromsø and were a part of the project "*Case Orrefjell*", sample details can be found in table *D1*, attachment *5.1 Sample Details*.

The produced water was, as mentioned, a part of Valeriya Mekhonina's master project *"Changes in Speciation and Kinetics of Po-210 in Produced Water from Oil Industry when mixed with Seawater",* and the produced water samples were from the Norwegian oil platform Troll C. The four produced water samples were prepared and measured: Blank (seawater), <10 kDa, <0.45 µm and Total (Meknonina, V. 2017).

The formation water-samples presented in this chapter were given by the Central Mining Institute of Silesian Centre for Environmental Radioactivity. Two parallels were measured, hereby be referred to as control water 1 and 2, respectively bottle 99 and 103. The Central Mining Institute in Poland performed all pre-treatment of the LRM prior to the treatment presented in this thesis (Bonczyk, M., Michalik, B. 2016).

The water samples presented below were prepared by the procedure presented in chapter *3.1.2 Procedure of Water Samples*. The water samples found in table 3 were prepared and measured;

Table 3. Water samples measured on ICP-QQQ for determination of ^{226}Ra.

Sample	Volume, L	1 mL ^{133}Ba added, ng/L	1 mL ^{133}Ba added, Bq/mL
Spiked Blank	2	-	-
0,001 Bq/L	2	9.30	88.0
0,01 Bq/L	2	9.30	88.0
0,1 Bq/L	2	9.30	88.0
Orrefjell 1	1.9	9.30	88.0
Orrefjell 2	1.8	9.30	88.0
Orrefjell 3	1.9	9.30	88.0
Orrefjell 4	2	9.30	88
Orrefjell 5	2	9.30	88.0
Produced Water – Blank	1	9.30	88.0
Produced Water - Total	1	9.30	88.0
Produced Water - < 0,45µm	1	9.30	88.0
Produced Water - < 10kDa	1	9.30	88.0
Control Water 1	2	9.30	88.0
Control Water 2	2	9.30	88.0

The standards and upconcentrated water samples were measured with semiconductor lens on ICP-QQQ.

3.2.4 Soil- and Sediment samples

Different soil samples were given to this master project. The soil from Orrefjell, 2.5-4.1, were a part of Schöpke, C. master project "*Uranium and Toxic Metal Uptake by the Earthworm Eisenia Hortensis in Contaminated Soils*" from 2017, whereas Orrefjell Control (O1-O3), were a part of project "*Case Orrefjell*". The alum shale was given to this master project, and the samples were a part of NPRA's project 603019, called "*Construction works in areas with sulphide containing rock – case: effects and environmental risks related to alum shale disposal site"* from 2016 (Skipperud et al. 2016).

The soil samples presented below were prepared by the full procedure presented in chapter *3.1.6 Procedure of Soil Samples*. The twelve samples of soil found in table 4 were tested, and had the following information:

Table 4. Soil Samples measured on ICP-QQQ for determination of ^{226}Ra in unknown environmental samples.

Sample	Comment	Weight, (g)	Acid solutions for digestion* (mL)		1 mL ^{133}Ba added	
			H_3PO_4	HNO_3	ng/L	Bq/L
Orrefjell 2.5	Homogenized soil 0% alum shale	5.01	25	12	18.4	176
Orrefjell 3.3	Homogenized soil 5% alum shale	5.01	25	12	18.4	176
Orrefjell 4.1	Homogenized soil 25% alum shale	5.01	25	12	18.4	176
Orrefjell Control 1, O1	Homogenized soil 14.9 ng ^{226}Ra/kg (548 Bq/kg)	5.01	25	20	18.4	176
Orrefjell Control 2, O2	Homogenized soil 14.9 ng ^{226}Ra/kg (548 Bq/kg)	5.00	25	20	18.4	176
Orrefjell Control 3, O3	Homogenized soil 14.9 ng ^{226}Ra/kg (548 Bq/kg)	5.00	25	20	18.4	176
Alum shale	Nordre road tunnel. No. 9354	5.02	25	12	18.4	176
CRM – IAEA 135	Sediment 653 pg ^{226}Ra/kg (23.9 Bq/kg)	1.00**	12,5	6	18.4	176
Blank 1		-	25	12	18.4	176
Blank 2		-	25	12	18.4	176
Blank 3		-	25	12	18.4	176
Blank 4		-	25	12	18.4	176

*The amount of HNO_3 in mL used depends on the content of organic matter present in the soil – HNO_3 was used to oxidize the organic matter present in the soil samples . The amount of H_3PO_4 remained constant for all soil samples digested except for CRM IAEA-135 due to a lower amount of substance used.

** Only 1 gram of the IAEA-135 was used due to limited amounts of the CRM.

The up concentrated soil samples were diluted ten times to a total volume of 5 mL prior to measurement on ICP-QQQ. The standards and soil samples were measured with X-lens on the ICP-QQQ.

3.2.4.1 Interferences – Matrix Effects

Soil samples and water samples with high conductivity have complex matrices, and it was desirable to obtain an idea of which other elements that might be present in the samples in addition to ^{226}Ra.

External standards were prepared by adding appropriate volumes of different standards to the appropriate concentrations, and can be found in table *E1*, attachment *6 "Which elements are present in the samples?"*

The produced water- and formation water samples were diluted ten times to a total volume of 5 mL, as done with the soil samples. The samples and standards were measured on ICP-QQQ with x-lens. An internal standard were prepared by diluting 0.5 mL 10 mg/L Rh with DI-water and 1 mL HNO_3 to a total volume of 50 mL – 100 µg/L Rh. The internal standard was added in line with a T-piece with the standards and diluted samples prior to the aerosol-formation within the ICP-QQQ.

3.2.4.2 Measurement of Soil Samples – NRPA Tromsø, Norway

The samples from Orrefjell; 2.5, 3.3, 4.1 and Orrefjell control-parallels, were measured by NRPA Tromsø using a Ge-detector, and the results were to be compared to verify the results of the new procedure. NRPA Tromsø performed a procedure were ^{226}Ra was measured by Ge-detector after reaching equilibrium with its daughters ^{214}Pb and ^{214}Bi. The activity of ^{226}Ra was calculated from the activity of 295 keV-and 352 keV-peaks of ^{214}Pb, and the 609 keV-peak of ^{214}Bi (Mauring, A. 2015).

4 Theoretical Background: Sample Preparation and Instruments

As mentioned in chapter *2.2.2 Radium-226*, there are two measurement techniques commonly used to determine ^{226}Ra in environmental samples; measuring the alpha radiation of ^{226}Ra by alpha spectrometry or by indirectly measure the alpha radiation of its progeny by Liquid Scintillation Counting. The recovery of the yield monitor, ^{133}Ba, is commonly measured by a Sodium Iodine-detector to determine the recovery of ^{226}Ra, but can also be measured by Liquid Scintillation Counting.

NaI-detector, Ge-detector and ICP-QQQ were used in this master project. The basic principles of the sample preparation and the instruments, will be described in relevance for ^{226}Ra in the following sub-chapters. The instrumental parameters of the instruments used in this master project can be found in attachment *1 Instrument Parameters*. The basic principles of alpha spectrometer and liquid scintillation counting (LSC) is referred to Advanced Physics Laboratory at University of Michigan "*Alpha Ray Spectroscopy*" from May 2005 and "*Chemistry and Analysis of Radionuclides – Laboratory Technique and Methodology"* by Hou, X. and Letho, J. p. 16-20 from 2012 for a more detailed explanation.

^{133}Ba will be referred to as a yield monitor when measured by emitted gamma radiation on Sodium Iodine-detector, whereas when measured on ICP-QQQ by its mass-to-charge ratio it will be referred to as an internal standard.

4.1 Microchemistry – Carrier and Yield Monitor

4.1.1 Trace Elements

In environmental samples the quantity of a radionuclide examined is nearly always very low, thus called trace amounts. The mass and the number of atoms of ^{226}Ra corresponding to 1 Bq activity is: $7.3*10^{10}$ atoms, $2.7*10^{-11}$ grams and $1.2*10^{-13}$ mol/L.

There is a risk that some of the matter will be absorbed onto surfaces, tools, particles and precipitates when dealing with trace amounts of a radionuclide. Adsorption in ion exchange and on glass surfaces takes place on the surface of silanol groups. These groups are weakly acidic, and the proton can dissociate in neutral or alkaline solutions. Thus, they can bind a metal ion. This will be illustrated by an example. If a glass contains 100 mL of a solution, where the concentration of the radionuclide is 10^{-7} mol/L, the whole content of the radionuclide can be absorbed into the surfaces of the beaker. Adsorption is a problem that must be considered during trace element analysis to avoid unreliable results (Hou, X. and Letho, J. 2012).

Adsorption can be avoided by the following methods. Radionuclides can be stored in acidic solution. By acidifying the solution, the cation Ra will be hydrated: $Ra(:OH_2)_6^{2+}$. The last method is to add a stable isotope of the same element to the radionuclide solution to such a large extent that the ion exchange sites of surfaces are saturated (Hou, X. and Letho, J. 2012). The last method exemplifies the use of carriers, which is an important tool in radiochemistry. The principle behind use of carriers will not be presented, but referred to "*Chemistry and Analysis of Radionuclides – Laboratory Technique and Methodology"* by Hou, X. and Letho, J. p. 28-30.

4.1.2 Yield Monitor

During a chemical separation, some of the radionuclide of interest may be lost and not recovered in the final sample used for measurement. To detect the amount of analyte recovered after sample preparations, a chemical yield is measured. The chemical yield is determined by using a carrier or a radioactive yield monitor. The carrier and the yield monitor can be isotopic or nonisotopic. For ^{226}Ra a nonisotopic yield monitor is used, since a suitable radioactive yield monitor of the same element is not available. ^{133}Ba is used for yield determinations for ^{226}Ra, and was used during this master project. ^{133}Ba is a gamma emitter, and decays by electron capture. It assumed that ^{133}Ba behaves chemically identical to ^{226}Ra, and in addition to behave chemically identical to ^{226}Ra, the measurement of ^{133}Ba will not interfere with the measurement of ^{226}Ra (Hou, X. and Letho, J. 2012).

4.2 Ion Exchange Chromatography

As mentioned in chapter *4.1 Microchemistry – Carrier and Yield Monitor*, the quantity of a radionuclide is nearly always in trace amounts in environmental samples. Thus, prior to measurement on an instrument, ICP-QQQ in this project, separation and up-concentration of the analyte is necessary. In this thesis, separation of the analyte and interfering compounds was performed by ion exchange chromatography. Up-concentration was performed by evaporation and re-dissolving the evaporated sample in a smaller volume with an appropriate acid.

The principle behind ion exchange chromatography will be briefly explained in relevance to ^{226}Ra, for a more detailed explanation see *"Ion Exchange Chromatography – Principles and Methods"* by Pharmacia Biotech, page 10-19. According to Pharmacia Biotech, ion exchange separation is:

> *"Separation in ion exchange chromatography depends upon the reversible adsorption of charged solute molecules to immobilized ion exchange groups of opposite charge."*
> Pharmacia Biotech, *"Ion Exchange Chromatography – Principles and Methods"*, p.10

^{226}Ra can be present with a positive charge (cation), and therefore, a resin with negative immobilized groups was used in this project.

The principle behind ion exchange chromatography is separation by the reversible adsorption of charged molecules/atoms, in this case cations, to immobilized ion exchange groups with opposite charge. Prior to application of sample, the resin is brought to equilibration where optimal pH and ionic strength is adjusted. This allows binding of the preferred cation, ^{226}Ra and ^{133}Ba, to the resin. After application of the sample, the cations carrying appropriate charge will bind reversibly to the resin. Inappropriate charged substances will be washed out of the column. By changing the conditions in the resin, substances can be removed from the column. In this project it is desirable to remove interfering elements like calcium, magnesium and strontium. It was not so desirable to remove cesium-isotope ^{133}Cs in order to measure ^{133}Ba on ICP-MS, since mass-shift on IPC-QQQ was used to "remove" this interfering element. By changing the ionic strength or changing the pH, substances are released in order of their binding strength (Pharmacia Biotech). The last step of the ion exchange separation in this project was to elute the analyte and yield monitor/ISTD.

4.3 Recovery and Blanks

4.3.1 Recovery

One of the first steps of method validation is the test of the whole procedure with pure reference compounds without any sample matrix, also referred to as a recovery test. By testing the whole procedure with a pure reference compound without sample matrix problems, such as loss of analyte during sample preparation can be detected and corrected for. The drawback with this test is influences of sample matrix and other compounds with comparable properties cannot be evaluated (Oehme, M.).

A known amount of reference compound can therefore be added to a real sample as the next step – also called spiking. The advantage of spiking a real sample is influences of sample matrix and other interfering compounds is induced. However, the samples have to contain no analytes or only low concentrations (Oehme, M.).

4.3.2 Blanks – Limit of Detection and Limit of Quantification

To estimate Limit of Detection and Limit of Quantification, blank samples, matrices with no detectable analyte, are measured. To determine whether the analyte was present in the sample, the sample signal is compared with the signal of the blank. In this project, blank samples were made and measured after each new "group" of samples. ^{133}Ba was added to the blanks as a yield monitor/ISTD, expect Spiking Blank. All method blanks should be prepared according to the procedure, in this case presented in chapter *3.1.2 Procedure of Water Samples* and *3.1.6 Procedure of Soil Samples*. The calibration blank should be measured on ICP-QQQ directly after preparation. The blanks can be used to check for contamination of instruments, and solvents used in the preparation of the sample and during analysis. The blanks used in this project is presented in table 5.

Table 5. Types of blank samples used in this master project.

Type of blank:	Method blank	Method blank	Method blank	Calibration blank
Group:	Spiked Orrefjell	Produced water	Soil Samples	Standards
Matrix:	DI-water	Seawater	-	DI-water
Number of blanks (N)	1	1	4	1

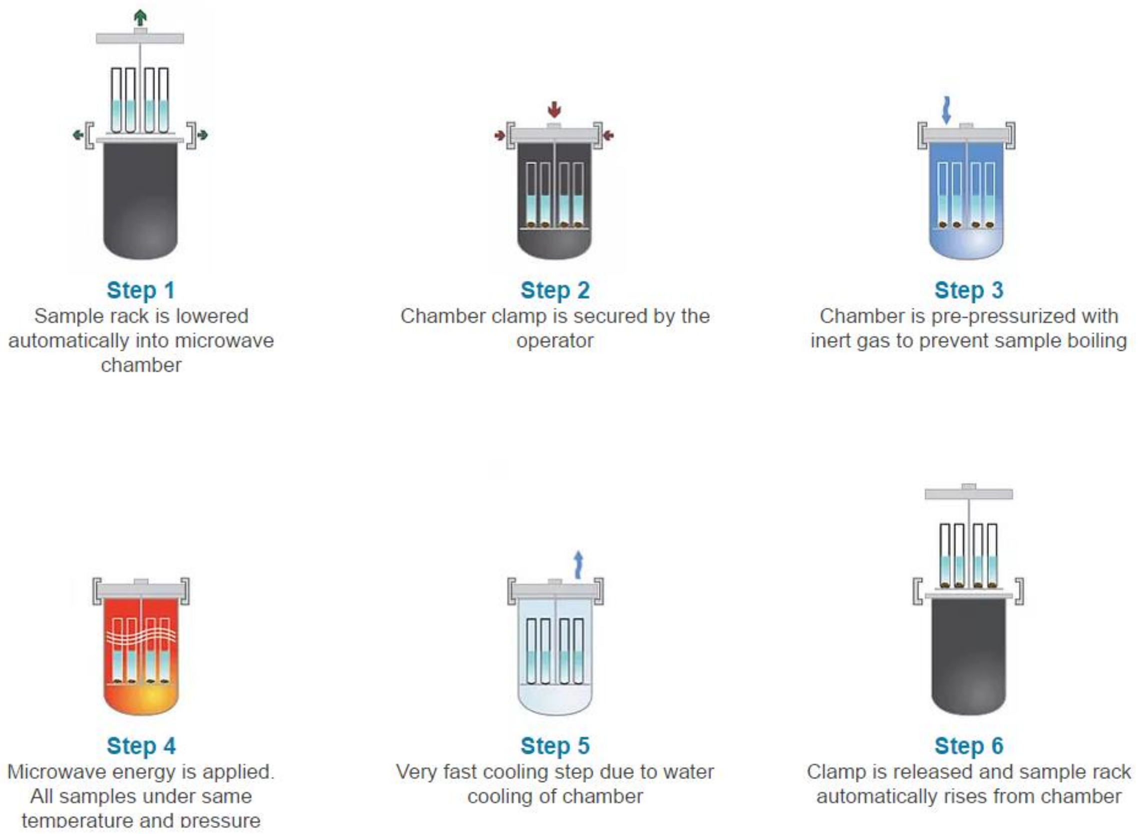
IUPAC recommends detection limit as "*that concentration which gives an instrument signal significantly different from the field blank*" (IUPAC. 1997). This means the smallest amount or concentration of an analyte that a method can detect with statistical confidence. It is important to distinguish between the detection limit for the method and the instrument. The detection limit for an instrument is often based on the analysis of the sample (often reagent blank) placed directly into the instrument, or on the signal to noise-ratio in a chromatogram. The detection limit for the method is based on the analysis of samples that have undergone the whole procedure, where the measurement results are used to calculate the LOD with the same equation as for the test samples (Magnusson, B., Örnemark, U. 2014).

The limit of quantification is defined at the minimum quantity of an analyte or compound, which can be reliably determined (Hayes, D. 2000).

4.4 UltraCLAVE for Acid Digestion of Soil Samples

As mentioned in chapter *3 Materials and Methods*, the soil samples needed further treatment prior to the separation on ion exchange. The resin requires the sample to be in liquid form. Digestion techniques can therefore be used to transfer the analyte, in this case ^{226}Ra, and matrix into solution. The use of acids like HCl and HNO_3 is called wet chemical digestion, and can be carried out in an open system (atmospheric pressure) or in closed vessels (Matusiewicz, H.) (Berghof Products). In this project a closed vessel was used with heating by a microwave oven. The principle of the UltraWAVE from Milestone will not be described in this thesis, but for information it is referred to Milestone Inc.'s brochure called "*UltraWAVE – The Game Changer in Microwave Digestion*".

The microwave digestion system used in this project is an UltraCLAVE IV from Milestone Inc. The UC from Milestone is described as a large reaction chamber where the chamber is pressurized with an inter gas prior to heating by microwaves. The chamber acts as a microwave and reaction vessel at the same time. The microwaves are introduced into the chamber through a microwave port which ensures a maximum efficiency regarding sample heating. The generated heat in the reactor is removed by a cooling system (Milestone Inc). According to Milestone's homepage, the UC can achieve speed, reproducibility, good quality of results and no cross contamination like any other microwave system. Figure 6 shows the process of UC.



Step 1
Sample rack is lowered automatically into microwave chamber

Step 2
Chamber clamp is secured by the operator

Step 3
Chamber is pre-pressurized with inert gas to prevent sample boiling

Step 4
Microwave energy is applied. All samples under same temperature and pressure

Step 5
Very fast cooling step due to water cooling of chamber

Step 6
Clamp is released and sample rack automatically rises from chamber

Figure 6. Process of UC (Milestone Inc.)

4.5 Inductively Coupled Plasma Mass Spectrometry – ICP-MS

4.5.1 ICP-MS in General

ICP-MS is considered as an ideal option for trace analysis, since it provides low detection limits and accurate and precise element data. The technique is relatively free of interferences, which is desirable when working with trace concentrations. The interferences which may be present is often be reduced or removed through the use of a gas filled cell operating in collision- or reaction mode (PerkinElmer).

The basic principles for ICP-MS will be explained briefly in this thesis, but a more detailed explanation is referred to *"The 30-minute Guide to ICP-MS – Technical Note ICP-Mass Spectrometry"* published by PerkinElmer. Other reference is Hou, X. and Letho, J. *"Chemistry and Analysis of Radionuclides – Laboratory Technique and Methodology"* p. 338-346 1st reprint 2012, and Hoffmann, E. and Stroobant, V. *"Mass Spectrometry – Principles and Applications"* p. 69-71. 3rd Edition 2012

ICP-MS is a measurement technique, which focuses on separation of isotopes according to their mass-to-charge ratio (*m/z*).

The sample, introduced as aerosol droplets into an argon plasma, is dried in the plasma. The molecules are also dissociated in the plasma, and electrons are removed from the components. Singly-charged ions are formed, and are directed into a mass filter, also referred to as the mass spectrometer. Most ICP-MS systems use a quadrupole mass spectrometer, which rapidly scans a mass range. With this technique only one mass-to-charge will be allowed to pass through the mass filter. For example, the quadrupole is set to allow ions with mass-to-charge ratio 226/1 to pass through, thus, ^{226}Ra will pass through the mass filter. However, other singly charged ions with equal mass, and doubly-charged with the double mass, will also pass through the mass filter. The ions will strike a dynode of an electron multiplier, a detector, upon exiting the mass filter. This releases a cascade of electrons, which are amplified and becomes a measureable pulse. The instrument compared the intensities of the measure pulse to the pulses of the standards. The standards make up an calibration curve, and is used to determine the concentration of the element of interest, which in this case is ^{226}Ra (PerkinElmer).

4.5.2 Agilent 8800 Triple Quadrupole

In this master project a triple quadrupole ICP-MS (ICP-QQQ) from Agilent Technologies was used. According to the IUPAC a triple quadrupole mass spectrometer is defined as:

> "Tandem mass spectrometer comprising two transmission quadrupole mass spectrometers in series, with a (non-selecting) RF-only quadrupole (or other multipole) between them to act as a collision cell."
>
> Vanhaecke, Frank for Agilent Technologies. September 2013. *Agilent 8800 ICP-QQ Application Handbook*. Page 5. Publication number 5991-2802EN, Agilent Technologies, Inc. 2013.

As mentioned briefly in chapter *4.5.1 ICP-MS in General*, singly charged ions can pass through a mass filter (Q_1) if the *m/z*-ratio is equal to the setting. For example it would not be possible to use ^{133}Ba as an internal standard if a single quadrupole is used. If Q_1 is set to 133 amu, it would not be possible to distinguish between the signal from ^{133}Ba and ^{133}Cs, since both elements will pass through. If Q_1 is set to 149 amu, barium oxide (^{133}Ba + ^{16}O) will pass through, but an interfering mass is ^{149}Sm^{+}. Thus, it would not be possible to distinguish between the two elements with single quadrupole ICP-MS.

Two separate steps for mass selection is provided by a ICP-QQQ, in this master project an Agilent 8800 ICP-QQQ. Q_1 is set to a given *m/z*-ratio, and only ions with this m/z-ratio is allowed through into the cell. Q_2 is set to another given *m/z*-ratio, and will only allow ions of interest from the cell through (Vanhaecke, F. 2013). In this master project Q_1 can be set to 133 amu, allowing $^{133}Ba^+$ and $^{133}Cs^+$ through into the reaction cell. Nitrous oxide is used as a reaction gas. ^{16}O from the reaction gas is believed to be transferred to $^{133}Ba^+$ forming $^{133}Ba^{16}O^+$ (149 amu). Q_2 is therefore set to 149 amu, and thereby only allowing $^{133}Ba^{16}O^+$ through. This approach provides control over the chemistry happening within the cell, and can solve problems from spectral overlap (Vanhaecke, F. 2013).

According to an article published by Larivière et al. in 2003 called *"Determination of Radium-226 in Environmental Samples by Inductively Coupled Plasma Mass Spectrometry after Sequential selective extraction"*, the polyatomic interferences that could be present when measuring ^{226}Ra includes $^{186}Os^{40}Ar$, $^{186}W^{40}Ar$, $^{208}Pb^{18}O$ and $^{207}Pb^{19}F$ – 226 *m/z*. It was assumed that by using nitrous oxide as a reaction gas, it would be possible to distinct between the signal from the polyatomic interferences and the analyte. ^{16}O from the nitrous oxide-gas would be transferred to Ra^+ and form RaO^+ (242 *m/z*). Agilent Technologies has published a technical overview for understanding oxygen (O_2) reaction mode in ICP-MS/MS for Agilent 8800 ICP-QQQ (Agilent Technologies. 2012). The principle behind the interactions between reaction gas, analyte and polyatomic interferences are the same for both oxygen and nitrous oxide. The polyatomic interferences would not interact with the nitrous oxide, thus making it possible to distinct between the signals of the analyte and polyatomic interferences. In standard mode (no gas) it is not possible to distinguish between the signal of analyte and signal of polyatomic interferences. It is worth to mention that ^{226}Ra is an earth alkaline metal, and can form $^{226}Ra^{2+}$, but during measurement on ICP-MS almost all ^{226}Ra will form $^{226}Ra^+$ - thus, reacting to radium oxide, not radium dioxide (252 *m/z*).

It was desirable to measure ^{133}Ba directly on the ICP-QQQ as an internal standard. Thus, making it possible to determine the recovery of the ISTD for the full procedure – sample preparation to complete measurement on ICP-MS. Ohno, T. and Muramatsu Y. published an article in 2014, called "*Determination of Radioactive Cesium Isotope ratios by Triple Quadrupole ICP-MS and its Application to Rainwater following the Fukushima Daiichi Nuclear Power Plant accident*". The study had an objective to determine the ratios of radioactive cesium, and Ohno and Muramatsu used nitrous oxide as reaction gas to reduce the isobaric interferences by barium to carry out determinations of Cs-ratios (Ohno, T, and Murumatsu, Y. 2014). In this article, nitrous oxide was used to reduce the interferences from barium isotopes. However, in this master project, nitrous oxide was used to reduce interference from the cesium isotope ^{133}Cs, as the Cs in non-reactive with nitrous oxide. The reactions between $^{226}Ra^+$, $^{133}Ba^+$ and nitrous oxide are displayed in figure 7.

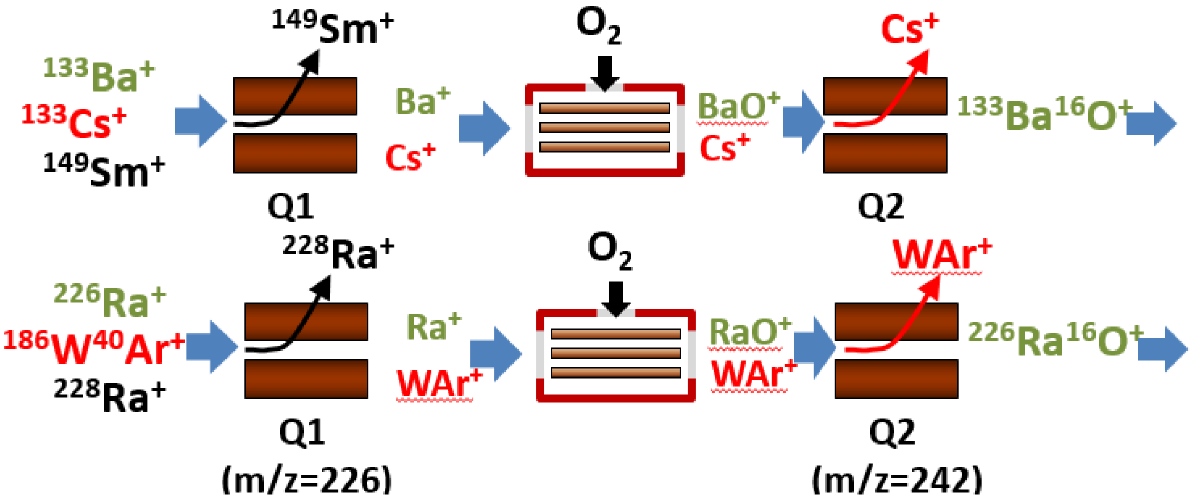


Figure 7. ICP-QQQ (Jensen, K. A, 2015)

4.6 Sodium Iodine Detector – NaI

The Sodium Iodine-detector is a solid scintillation detector, which is a detector used for gamma detection. The principle behind a NaI-detector will be briefly explained, but for a more detailed explanation see Hou, X. and Letho, J. "*Chemistry and Analysis of Radionuclides – Laboratory Technique and Methodology*" p. 20 1st reprint 2012.

The basic principle behind the detector is gamma rays absorbed in the inorganic crystal, which causes excitations in the crystal. Light emissions are produced when it's excitation states are relaxed, and the pulses are detected and amplified with a photomultiplier tube. The pulse is then directed through an amplifier to a multichannel analyzer, and an energy spectrum is created. The drawback of a solid scintillation-detector is a poor energy resolution. However, the advantage of a solid scintillation-detector is very good detection efficiencies. Large crystals enhance the detection efficiency of gamma rays (Hou, X. and Letho, J. 2012).

Radioactive decay is a random statistical process, so to decrease the uncertainty in the measurements, the samples will be measured once for a relatively long period of time. When a radioactive sample is measured, the certainty of the result increases with the number of counts registered and counting time. The relative uncertainties are lowered when the counting time increases (Pettersen, M. 2015).

As mentioned in chapter *4.1.2 Yield Monitor*, ^{133}Ba will be used as a yield monitor and internal standard for ^{226}Ra in this master project. ^{133}Ba is a gamma emitter, and the measurement of ^{133}Ba will not interfere with the measurement of ^{226}Ra. The yield recovery of the developed procedure will be measured by NaI-detector.

4.7 Germanium Detector – Ge

Germanium detectors are valuable tools to identify radionuclides in complex matrices like nuclear waste and environmental samples, because of the ability to analyze samples containing tens of gamma emitting radionuclides at the same time – which is not possible for NaI-detectors due to poor energy resolution (Hou, X. and Letho, J. 2012). The principle behind a Ge-detector will be briefly explained, but for a more detailed explanation see Hou, X. and Letho, J. "*Chemistry and Analysis of Radionuclides – Laboratory Technique and Methodology"* p. 20-21 1st reprint 2012.

A germanium detector is a semiconductor detector, which means that two semiconducting parts are attached together. An electric field is applied across the system in a reverse bias mode, which forms a region at the interface of the two semiconductors depleted with holes and electrons. Electron-hole pairs are formed when a gamma ray hits this depleted region, which in turn makes the system conducting. The electric field will produce an electric pulse that can be recorded (Hou, X. and Letho, J. 2012).

The Norwegian Radiation Protection Agency in Tromsø, use a procedure were ^{226}Ra is measured by Ge-detector after reaching equilibrium with its daughters ^{214}Pb and ^{214}Bi. The activity is calculated from the activity of 295 keV-and 352 keV-peaks of ^{214}Pb, and the 609 keV-peak of ^{214}Bi (Mauring, A. 2015).

5 Results and Discussion

In this chapter results from the experimental part of the project will be presented and discussed. The chapter will be divided into five parts; sample preparation, optimization of ICP-QQQ, determination of ^{226}Ra in unknown environmental samples, quality assurance and statistics, and last errors and further development.

5.1 Optimization of Sample Preparation

5.1.1 Sample Preparation – Transfer of Sample

As mentioned in the introduction, the goal for this thesis was to develop a procedure that was applicable for determination of ^{226}Ra in environmental samples. It was desirable to develop a method that was less time-consuming than the procedure with co-precipitation with $BaSO_4$, and avoid co-precipitation with $BaSO_4$ (Eichrom. 2003).

The procedure presented by Kim et al. in 1999 in the article "*Determination of ^{226}Ra in Environmental Samples using High-Resolution Inductively Coupled Plasma Mass Spectrometry*", was tested. Kim et al. (1999) added the ion exchange resin directly into the water sample after stirring the sample for three hours, and stirred the water sample with ion exchange resin for one additional hour before loading the sample with ion exchange resin onto the glass column (10 cm*1 cm).

The transfer of sample with cation exchange resin, with yield and analyte, was tried out in various ways. The techniques tried out were time-consuming and needed the worker’s attention at all times. This was to make sure the column did not run dry, and to pour additional water and resin onto the column. With these techniques it was difficult to work with more than one sample at the time. These techniques were not ideal for the Isotope Laboratory at NMBU, since it was desirable to measure more than one sample at the time.

Therefore, it was concluded to prepare the cation exchange resin directly onto the glass column and to use a Gilson MINIPLUS 3 Peristaltic Pump with four channels, with a low flow rate to pump all solutions through the column as shown in figure 8. The Gilson MINIPLUS 3 Peristaltic Pump is also available with eight channels, making it possible to work with several samples at once. The use of a Gilson MINIPLUS 3 Peristaltic pump made the procedure less laborious. However, the procedure was time-consuming, but overall the pump was considered beneficial due to less workload.

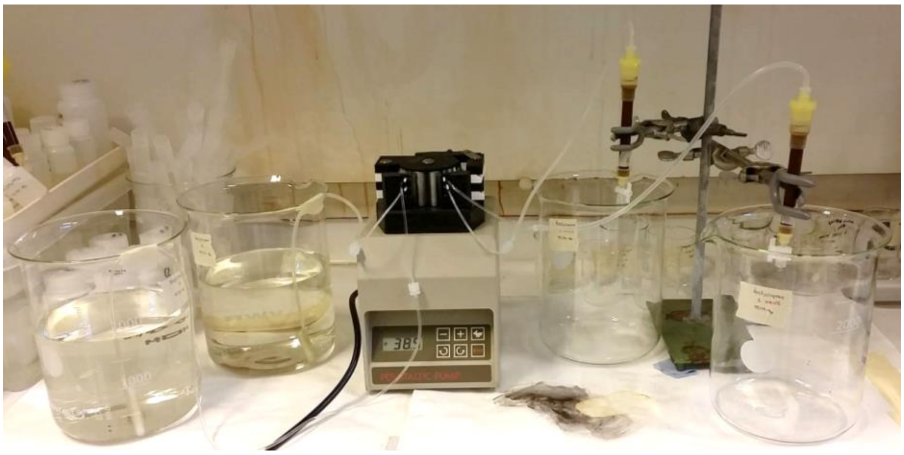


Figure 8. Transfer of two liter water sample through ion exchange resin using Gilson MINIPLUS 3 Peristaltic pump. Flow rate approximately 4 mL/min.

5.1.2 Recovery of ^{133}Ba in Different Matrices

The recovery test with DI-water and 9.30 ng/L ^{133}Ba was used to determine the optimal flow rate of the acid solutions used in ion exchange separation. Table 6 shows the results from this recovery tests, where the recovery of the yield monitor ^{133}Ba was measured on NaI-detector. The two samples, FW1-2, illustrate freshwater samples, whereas sample PW3 illustrates produced water.

Table 6. Recovery, in percentage, of ^{133}Ba detected in samples used for recovery testing measured on NaI-detector. A known activity of ^{133}Ba was added and no matrix was present. No ^{226}Ra present in solution. FW stands for freshwater, and PW stands for produced water. The table illustrates the presence of ^{133}Ba in upconcentrated sample, solvents used for ion exchange (IEX) and the loss of ^{133}Ba. "Recovery" illustrates the percentage of ^{133}Ba found in the sample solution, "IEX" illustrates the percentage of ^{133}Ba found in the ion exchange solutions, and "Loss" is the percentage of ^{133}Ba not found in the previous two groups. A total volume of 265 mL is used in the ion exchange separation – includes all solutions used. Significant figures: 2.

Sample	Recovery in Sample (%)	Sum of Recovery for all steps (%)	Loss of yield (%)	Recovery in IEX steps (%)	Flow rate (mL/min)
1 – FW	61	69	31	8.0	3.7
2 – FW	92	100	0.20	8.1	1.6
3 – PW	62	82	18	20	1.7

As seen from table 6, the two water samples illustrating freshwater samples had a recovery of 61% and 92%, respectively for FW1 and FW2. Different flow rates were tested, and table 6 displays the flow rate for the solutions through the column during the ion exchange separation. The recovery test of sample 1 had a flow rate of 3.7 mL/min, and had a recovery of 61% ^{133}Ba. Sample 2 had a recovery of 92%, flow rate 1.6 mL/min. By comparing these flow rates and recoveries, it was concluded that a flow rate of 1.6-2.0 mL/min was the optimal flow rate to obtain a recovery result over 70%, which was set as a lower limit prior to experiments. The article published by Kim et al. from 1999, used a flow rate of 2 mL/min during the ion exchange separation. A flow rate of 1.6-2.0 mL/min makes sure that the solvents have enough contact time with the resin material - enough contact time to exchange cations and elute the interfering cations as well as analyte and yield monitor/ISTD.

The recovery result for sample 3, illustrates the recovery of ^{133}Ba in produced water. Produced water has a more complex matrix compared to freshwater and seawater – salinity of 4.8% (w/V) (Mekhonina, V. 2017). As mentioned earlier, it was assumed that the recovery of ^{133}Ba would be lower for produced water compared to freshwater. The recovery of ^{133}Ba was found to be 62% in the sample solution, which is lower than the desirable 70% recovery. However, due to a complex matrix it was expected to be lower compared to a less complex matrix like freshwater, therefore a recovery result at 62% for the yield monitor was accepted.

5.1.2.1 Recovery of ^{133}Ba in Spiked Samples and Freshwater Samples

The solutions from the sample preparation of the spiked water- and Orrefjell samples were also measured to obtain a better estimate of the loss of yield, and analyte, in freshwater samples. The recovery measurements were performed for all water samples prepared in this thesis. This was to obtain a reliable recovery result for the procedure. To consider whether or not the procedure was optimal and well-functioning for its purpose, it was concluded that a recovery of at least 70% would be sufficient.

Table *B1* in attachment *3 Recovery Testing*, displays the recovery, in percentage, detected in the spiked samples and freshwater samples from Orrefjell. It also shows the average values for spiked samples, freshwater samples and the combination of the two sample groups – total. The results are visualized in figure 8, which shows the average results for spiked- and freshwater samples.

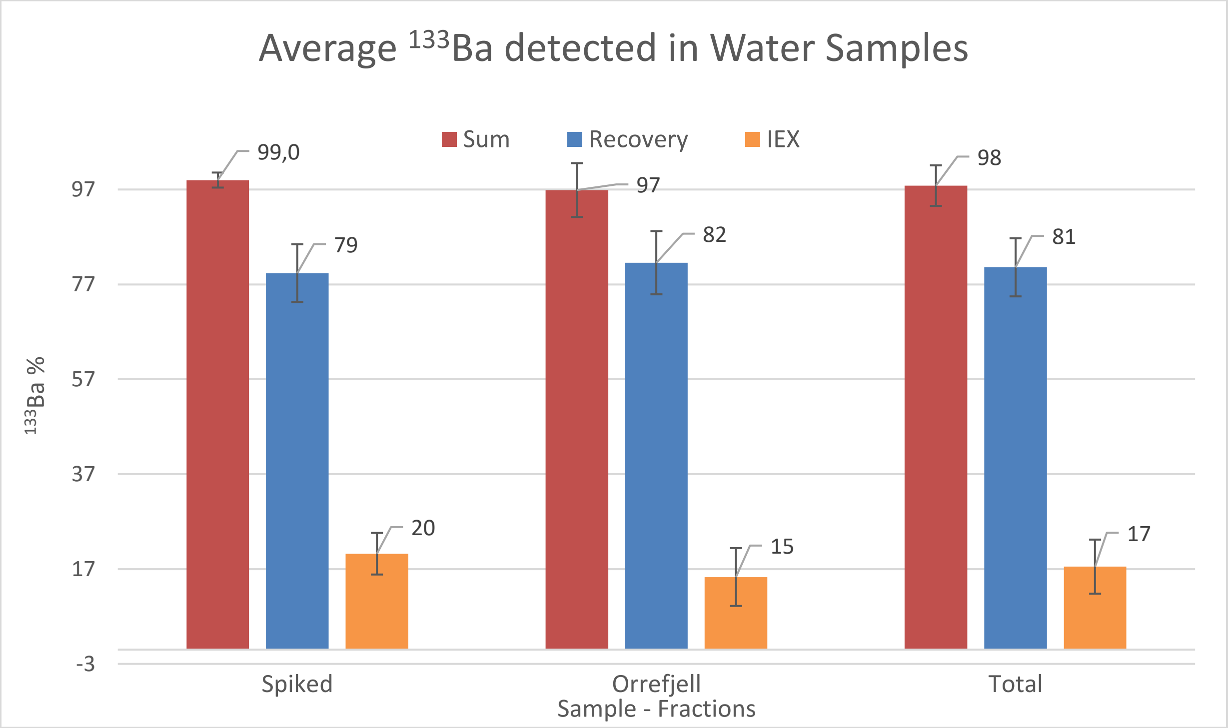


Figure 9. Average recovery in percentage of ^{133}Ba in spiked samples, freshwater samples from Orrefjell and the combination of the two sample groups. The standard deviation, in percentage, is also displayed. "Sum" illustrates the presence of ^{133}Ba found in sample solution and ion exchange-solutions, "Recovery" illustrates the percentage of ^{133}Ba found in the sample solution, and "IEX" illustrates the percentage of ^{133}Ba found in the ion exchange solutions. The yield monitor was measured on NaI-detector. Data can be found in table *B1*, attachment *3 Recovery Testing*.

Figure 9 shows an average recovery of 81 ± 6.1% ^{133}Ba in water samples with little or no matrix. This is well above the desirable 70% recovery, which was determined prior to preparations and measurements. An average loss of both yield monitor, and analyte, from 13 to 25% could be expected in presence of little or no matrix.

Figure 9 shows the presence of ^{133}Ba in the ion exchange-solutions for water samples with little or no matrix; 17 ± 5.7% of yield monitor, and thus, analyte, was lost during the cation exchange-separation. The recovery tests made it possible to determine the critical steps of the procedure, the critical stages of the ion exchange-procedure were 1.5M ammonium acetate and 3M hydrochloric acid. Ammonium acetate was used to remove interfering compounds like calcium, magnesium and strontium, whereas hydrochloric acid was used to wash out the EDTA-solution and the ammonium acetate-solution left in the column. The average presence of ^{133}Ba found the ammonium acetate-solutions for spiked samples and freshwater samples from Orrefjell was 7.2 ± 2.8%, whereas for 3M hydrochloric acid-solutions was 4.3 ± 0.69%. The sample preparation was not corrected and optimized for the loss of yield monitor and analyte during the sample preparation, however the effects of these steps has been taken into account when evaluating the further development of the procedure.

5.1.2.2 Recovery of ^{133}Ba in Produced Water- and Soil Samples

It was desirable to obtain recovery results for produced water- and soil samples as well. The recovery tests were performed for produced water and all soil samples presented and prepared in this thesis. Since the tests were performed for real environmental samples, influences of sample matrix and other compounds could be evaluated. The influences will be discussed later in chapter *5.3.3.4 Interferences – Matrix Effects*.

The results shown in this section were the following samples: produced water (blank, total, <0.45 µm and <10 kDa) and soil samples (Orrefjell 2.5, Orrefjell 3.3, Orrefjell 4.1, Orrefjell Control 1-3, alum shale, CRM IAEA-135 and Blank 1-4) (Mekhonina, V. 2017, Schöpke, C. 2017, Skipperud et al. 2016). These samples will be discussed later in chapter *5.3 Determination of ^{226}Ra in Unknown Environmental Samples* as well.

Table 7 displays the average recovery in percentage, detected in the produced water samples from Troll C and soil samples from Orrefjell, certified reference material IAEA-135 sediment and alum shale. These samples have a more complex matrix compared to freshwater samples; thus, the recovery in these samples was expected lower than freshwater-recoveries.

Table 7. Average values of ^{133}Ba, yield monitor, measured on NaI-detector for produced water- and soil samples. The blank samples are not taken into account when calculating these values. The flow rate for the samples were 1.6 mL/min. Significant figures: 2. Data can be found in attachment *3 Recovery Testing*, table *B2* .

Sample	Recovery (%)	STD (%)	Sum of Recovery (%) for all steps	STD Sum (%)	Loss of yield (%)	STD Loss (%)	Recovery of IEX steps (%)	STD IEX (%)
Average Produced Water	**57**	5.3	**81**	7.5	**19**	7.5	**24**	2.3
Average Soil	**62**	36	**71**	39	**29**	39	**8,6**	7.4
Average Soil*	**81**	11	**92**	4.0	**8,0**	4.0	**11**	7.4

*Average and standard deviation were calculated without soil sample 4.1 and alum shale.

As seen in table 7, the average recovery of ^{133}Ba in produced water samples was 57 ± 5.3%, whereas for freshwater samples the average was 81 ± 6.1%. Hence, the assumption was correct – a more complex matrix influences the recovery of the yield monitor, and the analyte ^{226}Ra. This means that a loss from 37-48% on average could be expected according to these results. However as seen in table 7, there was 19 ± 7.5% of the yield monitor that was not found in either sample solution or solutions from the ion exchange solutions – 24 ± 2.3% of the yield monitor was detected in the ion exchange solutions.

As mentioned previously, some steps of the ion exchange procedure were more critical, like 1.5M ammonium acetate and 3M hydrochloric acid. For produced water the average presence of ^{133}Ba in ammonium acetate was 12 ± 1.7%, and 4.8 ± 0.9% of ^{133}Ba was found in the hydrochloric acid-solutions on average.

As seen from table 7, the average recovery of ^{133}Ba in soil samples was 62 ± 36% if soil sample 4.1 and alum shale were included. These two samples had a recovery of 4.9% and 5.7% respectively for soil sample 4.1 and alum shale, which greatly affects the average value and standard deviation. Soil sample 4.1 consists of approximately 25% alum shale. As presented in chapter *3.1.4 Digestion and Sample*

Preparation of Soil Samples, the soil sample-solutions were diluted to approximately two liters, pH 2, after filtration. The samples were loaded onto the ion exchange column with a specific pH binding ^{133}Ba and ^{226}Ra to the resin. A change in pH over time could cause the low recovery in these two samples. A test to check the changes in pH over time should have been performed to verify this theory, but was not performed.

If the two low recovery-samples were excluded, the average recovery of ^{133}Ba was 81 ± 11%. The recovery of ^{133}Ba detected in the different fractions; upconcentrated sample (recovery), ion exchange solutions (IEX) and the loss (loss) can be seen in figure 10. Figure 10 illustrates the effect of the two samples, soil sample 4.1 and alum shale, on the average and standard deviation.

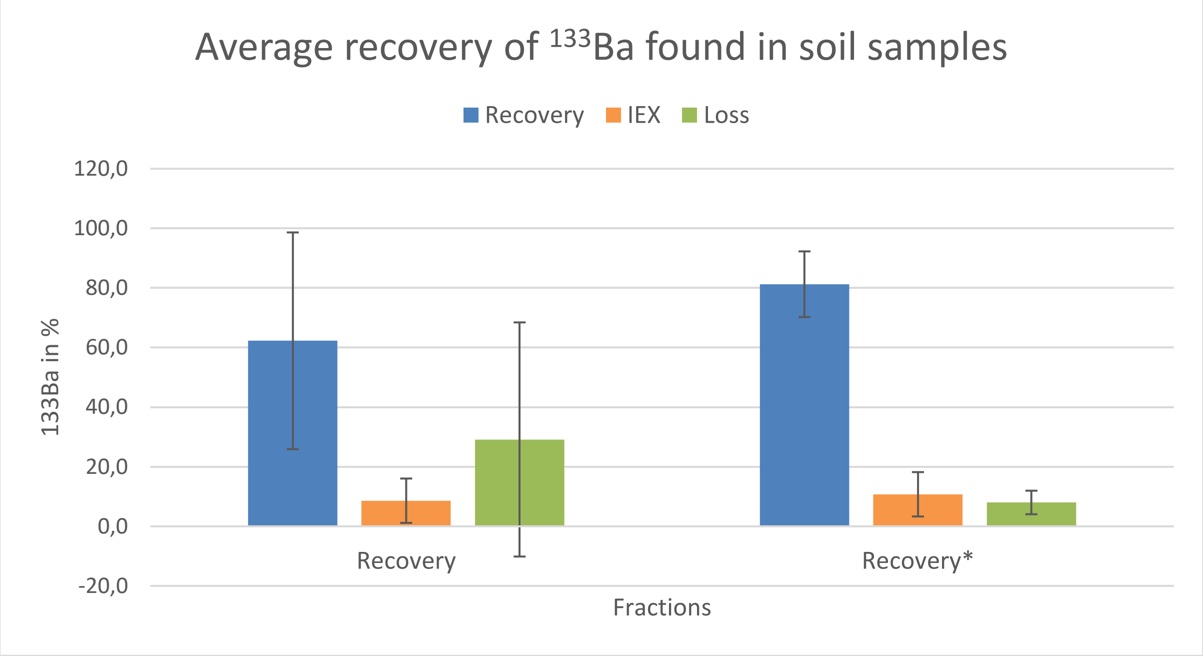


Figure 10. Average recovery in percentage of ^{133}Ba in soil samples. "Recovery" represents the average where soil sample 4.1 (25% alum shale) and alum shale is included, whereas "Recovery*" represents the average where soil sample 4.1 (25% alum shale) and alum shale is excluded. The standard deviation, in percentage, is also displayed. "Recovery" illustrates the percentage of ^{133}Ba found in the sample solution, "IEX" illustrates the percentage of ^{133}Ba found in the ion exchange solutions, and "Loss" is the percentage of ^{133}Ba not found in the previous two groups. The yield monitor was measured on NaI-detector.

As illustrated by figure 10, the two samples containing high amounts of alum shale greatly affected the average value of yield monitor recovery. According to the average value and standard deviation, the recovery of ^{133}Ba, and thus, ^{226}Ra, ranged from 26% to 99% in the up concentrated soil sample. However, by excluding the two samples the recovery could be expected to range from 70% to 92% according to these results.

It is important to mention the 89% recovery of the certified reference material IAEA-135, and only 4.9% of the yield monitor was lost – not found in either sample solution or ion exchange-solutions. The weighed in amount of IAEA-135 was 1.0 gram, whereas for the other soil samples 5 grams were used. A good recovery for the CRM can perhaps be explained by a unsaturated resin material.

As with the water samples, the most critical steps during the ion exchange separation were ammonium acetate and 3M hydrochloric acid. The average amount of ^{133}Ba detected in ammonium acetate was

5.2 ± 5.7%, whereas for 3M hydrochloric acid the average amount of ^{133}Ba was 1.7 ± 1.3% – both soil sample 4.1 and alum shale sample were included in these calculations. The average amount of ^{133}Ba detected in these two steps combined were 3.4 ± 4.4%. The sample preparation was not corrected and optimized for the loss of yield monitor and analyte during these steps, however the effects of these steps has been taken into account when evaluating the further development of the procedure.

5.1.3 Digestion of Soil Samples

This section of the chapter focuses on the tests performed to find the optimal digestion technique for soil samples concerning barium- and radium sulphate.

The first test with either HNO_3, HF and HCl or HNO_3 and HCl did not work as desirable due to low recovery of Ba. Further experiments was performed with other acid solutions was performed to find the optimal digestion technique for soil samples.

The measurement of the seven certified reference materials, GWB07401, GBW07403, NCS DC 73325, NCS ZC 73007, NIST 2709a, NIST 2710a and NIST 2711a, digested with HNO_3/H_3PO_4 and $HNO_3/H_3PO_4/HBF_4$ on UW gave the results presented in table 8, both in mg/kg and percentage of the certified value.

Table 8. mg/kg and % barium measured by ICP-MS after digestion with two different acid-solutions; HNO_3/H_3PO_4 and $HNO_3/H_3PO_4/HBF_4$. Certified values for each certified reference material is also given. Data can be found in table *C2* and *C3*, attachment *4 Digestion of Soil Samples*. Significant figures: 2

				Ba	
LOD (w/w)				0.10	
LOQ (w/w)				0.36	
Sample Name	**CRM**	**Certified Value**	**Acid Solution**	**[mg/kg]**	**%**
A1	GBW 07401	590 ± 15	$HNO_3/H_3PO_4/HBF_4$	600	100
A2	GBW 07401	590 ± 15	HNO_3/H_3PO_4	650	110
A3	GBW 07403	1200 ± 30	$HNO_3/H_3PO_4/HBF_4$	1200	97
A4	GBW 07403	1200 ± 30	HNO_3/H_3PO_4	1300	100
A5	NIST 2710a	790 ± 36	$HNO_3/H_3PO_4/HBF_4$	760	97
A6	NIST 2710a	790 ± 36	HNO_3/H_3PO_4	770	97
A7	NIST 2711a	730 ± 15	$HNO_3/H_3PO_4/HBF_4$	740	100
A8	NIST 2711a	730 ± 15	HNO_3/H_3PO_4	690	94
A9	NCS DC 73325	180 ± 27	$HNO_3/H_3PO_4/HBF_4$	180	100
A10	NCS DC 73325	180 ± 27	HNO_3/H_3PO_4	180	100
A11	NCS DC 73007	410 ± 18	$HNO_3/H_3PO_4/HBF_4$	400	98
A12	NCS DC 73007	410 ± 18	HNO_3/H_3PO_4	390	95
A13	NIST 2709a	980 ± 28	$HNO_3/H_3PO_4/HBF_4$	980	100
A14	NIST 2709a	980 ± 28	HNO_3/H_3PO_4	950	97

As presented in table 8, both acid-solutions could be used for the digestion of soil samples containing barium sulphate. As mentioned earlier, it was desirable to use a digestion method that was applicable and robust to several types of minerals. As seen for table 8 the average recoveries of Ba in samples digested with only HNO_3 and H_3PO_4 were ranging from 94 to 110% of the certified values. The recovery of Ba in CRM digested with HNO_3, H_3PO_4 and HBF_4 ranged from 97 to 100% of the certified values.

HBF_4 produces toxic and corrosive fumes (including HF and other fluorine compounds) when digested (Pubchem). If using HBF_4, an inert spray chamber within the ICP-QQQ is also needed. Therefore, the acid-solution that was used further in digestion of soil was HNO_3/H_3PO_4. The safety aspects can justify the use of HNO_3/H_3PO_4 as acid-solution for further analysis of soil samples.

It is worth to mention that there are other methods to dissolve barium sulphate, for example fusion. Fusion is often considered a better technique for digestion of relatively insoluble compounds compared to microwave high-temperature digestion. However, it is also worth to mention that fusion is often considered more laborious compared to a leaching approach, and contamination of sample by impurities in the reagent is quite possible due to large quantities of the flux required. There may be problems with the aqueous solutions resulting from fusions, since the solutions will have a very high salt content – which is not desirable when working with ion exchange-separation (MARLAP. 2004). Fusion was not an option while working with this master thesis, due to lack of necessary instruments.

5.1.3.1 Digestion of Rare Earth Elements (REE)

The Rare Earth Elements, REE, are a moderately abundant group, consisting of 17 elements in the periodic table. This group includes the 15 lanthanides, scandium and yttrium. The rare earth elements are moderately abundant in the Earth´s crust – cerium being the 25th most abundant element. In rock minerals, the elements tend to occur in compounds as trivalent cations in oxides, carbonates, phosphates and silicates (REE Handbook). The elements has similar properties, and are often treated as a group rather than individuals. The rare earth elements are considered insoluble in sodium hydroxide, NaOH, and HN_4OH, and readily soluble in HNO_3 and HCl. The rare earth element oxides, hydroxides, carbonates, fluorides, oxalates, sulfates and phosphate are all considered insoluble in water and neutral to basic media (Inorganic Ventures).

ICP-MS is the preferred measurement technique for rare earth elements, because the mass interferences are far less of a problem than with spectral emission interferences in Inductively Coupled Plasma Optical Emission Spectrometry, ICP-OES.

Determination of the rare earth elements was not a part of this master thesis. However, it is worth to mention that digestion with microwave high pressure UltraWAVE at 260˚C for 40 minutes with both acid-solutions, HNO_3/H_3PO_4 and $HNO_3/H_3PO_4/HBF_4$, gave very accurate and precise results for almost all the rare earth elements. The results for the element present in the certified reference material corresponded well with the certified reference values given in the certificate. Rare earth elements are considered less soluble than barium sulphate, thus also radium sulphate. Since the rare earth elements dissolved well using HNO_3/ H_3PO_4 and $HNO_3/ H_3PO_4 /HBF_4$ in UltraWAVE, it was assumed that radium sulphate will dissolve as well. The data will not be discussed any further, but can be found in attachment *4 Digestion of Soil Samples*, table *C4* and *C5*.

5.2 Optimization of ICP-QQQ

Prior to measurement of environmental samples containing ^{226}Ra, the instrument was optimized. Two different gas-modes were tested to optimize the measurements on ICP-QQQ: no gas and nitrous oxide. The instruments parameters can be found in attachment *1.1 Inductively Coupled Plasma Mass Spectrometry*.

Several types of samples were prepared for optimization of the instrument parameters on ICP-QQQ. This includes the spiked water samples with known concentrations of ^{226}Ra, freshwater samples from Orrefjell and standards with known concentrations of ^{226}Ra. The samples and standards had known concentrations of the yield monitor/ISTD ^{133}Ba. The spiked samples and freshwater samples from Orrefjell were used for estimation of recovery of yield monitor, see chapter *5.1.2 Recovery and Spiking*. The recovery of ^{133}Ba, was measured on NaI-detector prior to measurement on ICP-MS, to see if the measurements between the two instruments corresponded.

5.2.1 Gas mode – Nitrous oxide or no gas

Two gas modes were tested on the ICP-QQQ: no gas and nitrous oxide. With the use of nitrous oxide as reaction gas, it was believed that ^{16}O would transfer from nitrous oxide to ^{226}Ra$^+$, and form ^{226}Ra^{16}O$^+$, radium oxide, with a mass of 242. The polyatomic interferences would not react with nitrous oxide, and thus, it was possible to distinguish between the signal attributable to the analyte and interferences.

Prior to measurement of samples with ^{226}Ra, the impact of interferences on the cps-values were tested with the two different gas modes. As mentioned in chapter *4.5.2 Agilent 8800 Triple Quadrupole*, ^{186}Os^{40}Ar, ^{186}W^{40}Ar, ^{208}Pb^{18}O and ^{207}Pb^{19}F could be polyatomic interferences for ^{226}Ra-determination on ICP-MS (Larivière et al. 2003).

Table *D2* in attachment *5.1 Measurement of Polyatomic Interferences*, shows the measurement of ^{133}Ba and ^{226}Ra in presence of interfering compounds (polyatomic interferences). A low signal of ^{133}Ba and ^{226}Ra would indicate little or no interference from possible interfering compounds, since no ^{133}Ba and ^{226}Ra were added to these solutions.

As seen from table *D2* lead, cesium and tungsten had low counts per second, leading to a low concentration with a high relative standard deviation when using N_2O as reaction gas. The concentrations are below the limit of detection, thus, noise is measured leading to a high relative standard deviation. As mentioned previously, Cs could be a interfering mass for Ba – however, as seen in table *D2* the counts for Cs was 0,6 cps if N_2O was used a reaction gas. When using the gas mode no gas, it was clear that Cs was a huge interference for ^{133}Ba. As seen in table D2, the estimated concentrations of Pb and W were estimated to be respectively 500 and 1400 pg/L when measuring ^{133}Ba. This indicates contamination of ^{133}Cs in the standards, since Pb has a mass of 207 amu and W has a mass of 184 amu – polyatomic interferences are impossible for higher masses, unless there are doubly charged interferences. Pb and W do not form doubly charged interferences for 133 amu. If no gas was to be used it was also important to surveil ^{186}W^{40}Ar, but it was not possible to use ^{133}Ba as an ISTD in this gas mode. The standards 71A, 71B and 71D include almost every element in the periodic table as shown in chapter *3.1.1 Materials for Developed Method – Water and Soil.* A low cps-value, 0.04 cps with N_2O as reaction gas, indicated little or no interference from the elements present in these standards. According to these results, it was concluded that Pb, Cs and W did not interfere with the measurement of barium and radium when using nitrous oxide as reaction gas.

5.2.2 Recovery of ^{133}Ba on ICP-MS

The recovery of ^{133}Ba has been measured on both NaI as yield and ICP-MS as internal standard. Figure 11 illustrates the results of recovery percentage of ^{133}Ba measured on both NaI and ICP-QQQ. The difference in recovery measured on NaI and ICP-MS for the same samples is illustrated in this figure.

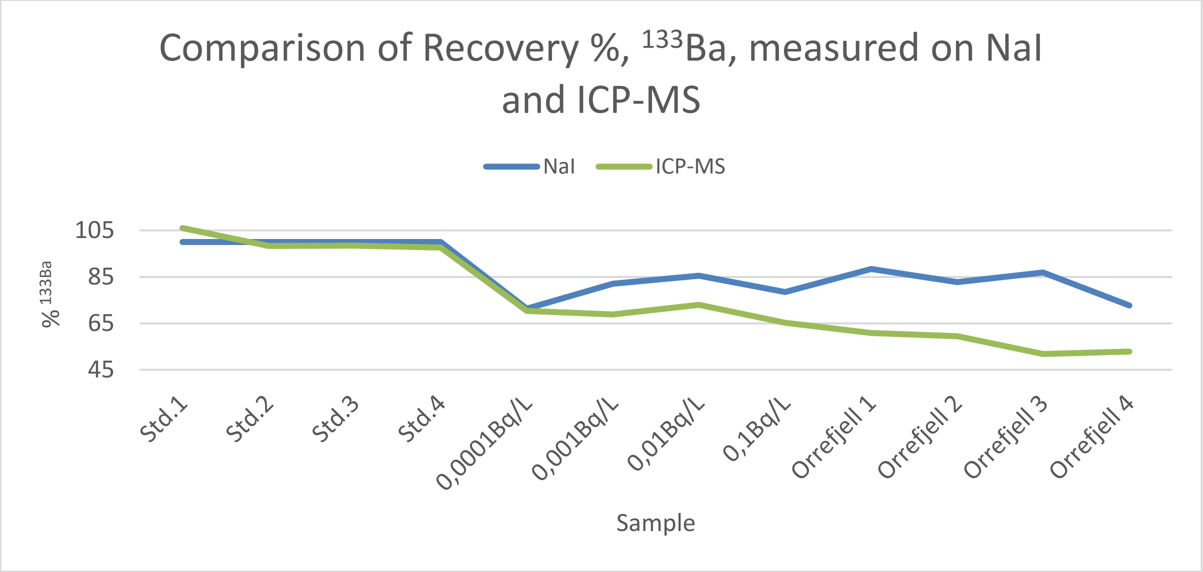


Figure 11. Measured ^{133}Ba recovery, in percentage, by NaI and ICP-QQQ. Data found in table *D4*, attachment *5 Determination of ^{226}Ra in Unknown Environmental Samples*.

Figure 11 illustrates the recovery of ^{133}Ba detected in the two instruments; NaI and ICP-QQQ. The recovery of ^{133}Ba ranged from 52-73% for the spiked samples and freshwater samples when measured on ICP-QQQ, whereas the recovery measured on NaI ranged from 71-88%.

If the recovery of ^{133}Ba was measured directly on ICP-QQQ compared to NaI-detector, it was the possibility to detect matrix effects present within ICP-QQQ. Thus, making it possible to determine the recovery of the ISTD for the full procedure – sample preparation to complete measurement on ICP-QQQ. This cannot be detected if the recovery is measured and determined by NaI-detector, since the recovery is determined prior to analysis on ICP-MS. The detection of matrix effects happening within the ICP-MS can explain the difference in measured recovery between the two instruments NaI and ICP-MS, shown in figure 11. Other possible sources leading to the difference can be drift within the ICP-QQQ. Standard 3, 500 pg ^{226}Ra per liter, was used as a drift check for every fifth sample measured on ICP-QQQ. The measurements indicated that there was a drift in the instrument, and the estimated concentrations had to be corrected for this systematic error in repeatability. The results for ^{133}Ba presented in this figure are not drift corrected, by the results of ^{226}Ra presented later in this thesis are drift corrected. By correcting for the estimated concentrations for the drift, the concentrations of the samples would not be affected by this systematic error. It was assumed that preconditioning of the instrument prior to measurement, would decrease the possibility of changes in the instrument's reading over extended periods. It was also assumed that measuring samples with two gas modes simultaneously would increase the drift in the instrument. Thus, by using only nitrous oxide as gas mode, it was assumed that the changes in the instrument's reading over time would decrease – giving more accurate results for both ^{133}Ba and analyte, ^{226}Ra.

Thus, by determining the recovery of yield with NaI, it was not be possible to detect the effects within the ICP-MS. It was desirable to measure the recovery of the ^{133}Ba-monitor directly on the ICP-QQQ. Eliminating the measurement of the yield monitor on NaI-detector, makes the duration of complete analysis shorter – which is desirable if there is a need for urgent results. The preferred gas mode was therefore be nitrous gas, even though this is not a conventional gas mode used on ICP-QQQ.

5.3 Determination of ^{226}Ra in Unknown Environmental Samples

It is important to mention again that this was a method development project, thus, the three next chapters will focus on various quantification criteria like LOD, LOQ, reliability and systematic errors. The concentration of ^{226}Ra will be quantified, but the concentrations will be discussed in relevance for the goal – *develop a method* to determine ^{226}Ra in environmental sample on ICP-QQQ. This chapter will focus on unknown environmental samples. Thus, both water- and soil samples are measured. An independent method was used for verification of the results and the method, and the results will be presented later in this chapter.

5.3.1 Standard Curve

The results of the standards were used to create a standard curve and an equation used for quantification of ^{226}Ra in unknown environmental samples. The standards were measured with N_2O as gas mode and corrected with ^{133}Ba as ISTD. The standard curve is presented in figure *D1*, attachment 5 *Determination of ^{226}Ra in Unknown Environmental Samples.* The y-axis represents (cps ^{226}Ra/cps ^{133}Ba) whereas the x-axis represents the concentration of ^{226}Ra in pg/L. The instrumental detection limit was determined to be 0.69 pg ^{226}Ra/L and the background equivalent concentration, BEC, was determined to be 0.17 pg/L. The BEC-value indicates the instruments ability to distinguish an element signal from the background, and the lower the value, the easier it is to distinguish between element- and background signal (Whitehead. Paul 2015).

5.3.2 Limit of Detection and Limit of Quantification

The limit of detection was determined using the results from produced water blank (PW Blank), Soil Blank 2, 3, and 4. The results are displayed in table *D1*, attachment *5 Determination of ^{226}Ra in Unknown Environmental Samples* . The limit of quantification is displayed in the table 9. The detection limit is calculated by three times the signal-to-noise ratio of the method blanks, and quantification limit is calculated by ten times the signal-to-noise ratio of the method blanks. The detection limit and quantification limit displayed in the table represents the LOD and LOQ for both water- and soil procedure.

Table 9. Limit of Detection and Limit of Quantification in pg/L ^{226}Ra, measured with S-lens. The concentrations are corrected with ^{133}Ba as internal standard. Limit of Detection and Limit of Quantification is presented for both ^{226}Ra and ^{228}Ra in start volume or start weight. Results for ^{226}Ra is given with two significant figure, whereas ^{228}Ra is given with one significant figure . Data can be found in attachment *5.2 Water Samples*, table *D1*.

	^{226}Ra → ^{242}Ra [pg/L]	^{226}Ra → ^{242}Ra [pg/kg]	^{228}Ra → ^{244}Ra [pg/L]	^{228}Ra → ^{244}Ra [pg/kg]
LOD:	0.020	7.8	0.0003	0.1
LOQ:	0.064	26	0.0009	0.4

As seen from table 9, the limit of detection was determined to be 0.020 pg/L ^{226}Ra for water procedure, and 7.8 for soil procedure – Soil Blank 1 was excluded. Soil blank 1 had 16 pg/L ^{226}Ra with a relative standard deviation 10%, which was not desirable considering it was a blank sample. Ideally, the blank should contain as little or no analyte to obtain a low detection limit.

As mentioned in the introduction, USEPA requires a detection limit lower than 1 pg ^{226}Ra/L (0.4 Bq/L) for the analytical method applied for analysis of drinking water (Park, C. J. et al, 1998). Thus, according to these results the method can be applied for analysis of drinking water. The limit of quantification was determined to be 0.064 pg/L ^{226}Ra for water, and 26 pg/kg ^{226}Ra for soil.

The limit of detection and –quantification for ^{228}Ra has been estimated from ^{226}Ra-results. The limit of detection was estimated to be 0.0003 pg/L for water and 0.1 pg/kg for soil, whereas the limit of detection was estimated to be 0.0009 pg/L ^{228}Ra and 0.4 pg/kg respectively for water and soil procedure. This was not tested with standards containing ^{228}Ra, just estimated from the results of ^{226}Ra.

5.3.3 Determination of ^{226}Ra in Environmental Samples

5.3.3.1 Water Samples – Freshwater and Produced Water

The water samples presented in this section are both freshwater samples and produced water samples. The results were corrected with both yield and ISTD. The spiked samples and Orrefjell 1-4 were measured two separate times to check the repeatability and to optimize the instrument parameters. Orrefjell 5, produced water- and formation water samples were only measured once as unknown sample.

Table 10 shows the concentration of ^{226}Ra in the water samples measured with S-lens on ICP-QQQ. The table shows results corrected with ISTD and yield.

Table 10. Concentrations of ^{226}Ra in pg/L and Bq/L in water samples. The table shows concentrations in start volume corrected with ISTD and yield. Significant figures: 2.

Sample	Start Volume (mL)	ISTD [pg ^{226}Ra/L]	ISTD [Bq ^{226}Ra/L]	YIELD [pg ^{226}Ra/L]	YIELD [Bq ^{226}Ra/L]
0.001 Bq/L	2000	0-048	0.0018	0.039	0.0014
0.01 Bq/L	2000	0.32	0.012	0.25	0.0091
0.1 Bq/L	2000	3.2	0.12	2.6	0.095
Orrefjell 1	1900	0.14	0.0051	0.12	0.0044
Orrefjell 2	1800	0.14	0.0051	0.12	0.0044
Orrefjell 3	1900	0.34	0.012	0.26	0.010
Orrefjell 4	2000	0.083	0.0030	0.063	0.022
Orrefjell 5	2000	0.37	0.014	0.28	0.010
K1	2000	150	5.5	110	4.0
K2	2000	160	5.9	120	4.4
PW 10 kDa	1000	27	0.99	12	0.44
PW 0.45 µm	1000	25	0.91	12	0.44
PW total	1000	22	0.80	14	0.51

As seen from table 10 the concentration of ^{226}Ra ranged from 0.083 to 0.37 pg/L in samples from Orrefjell when corrected with ISTD, whereas it ranged from 0.063 to 0.28 pg/L when corrected with yield. The produced water samples ranged from 22-27 pg/L when ISTD-corrected and 12-14 pg/L when corrected with yield. According to the results the highest concentrations of ^{226}Ra was found in produced water (>10 kDa) when corrected with ISTD – 27 pg ^{226}Ra/L.

The formation water sent from Central Mining Institute of Silesian Centre for Environmental Radioactivity had the greatest concentration of ^{226}Ra of all water samples, 150 and 160 pg/L respectively for K1 and K2, when corrected with ISTD. The two samples were parallels, and were supposed to have equal concentrations. The evaluation report published by Michal Bonczyck and Boguslaw Michalik in April 2016, showed that the average activity in this water was 100 ± 26 pg/L ^{226}Ra (3.7 ± 0.95 Bq/L) (Bonczyk, M., Michalik, B. 2016). Ten results of ^{226}Ra concentration had been reported, and the results varied from 55 to 130 pg/L ^{226}Ra (2.0 Bq/L-4.8 Bq/L). The concentrations presented in this thesis are greater compared to the mean-value reported by Michal Bonczyck and Boguslaw Michalik (Bonczyk, M., Michalik, B. 2016). The correction with ISTD overestimated the concentration (150-160 pg/L), whereas yield-corrections were within the area of previously measured concentrations(110-120 pg/L).

5.3.3.2 Soil Samples

The soil samples presented in this section are both soil from Orrefjell (O1-O3), soil samples mixed with alum shale (2.5-4.1), pure alum shale and certified reference material IAEA-135

Table 11 shows the concentration of ^{226}Ra in soil samples measured with X-lens on ICP-QQQ. The table shows results corrected with ISTD and yield, and dilution prior to measurement on ICP-MS was also corrected for.

Table 11. Concentration of ^{226}Ra, µg/kg and Bq/kg, in soil samples from Orrefjell, alum shale and Certified Reference Material IAEA-135. All results are given with two significant figures**.** The results are corrected for dilution and mass.

Sample Name	Weight, g	ISTD [µg ^{226}Ra/kg]	ISTD [Bq ^{226}Ra/kg]	YIELD [µg ^{226}Ra/kg]	YIELD [Bq ^{226}Ra/kg]
Orrefjell 1	5.0	150	530	130	480
Orrefjell 2	5.0	150	530	160	570
Orrefjell 3	4.9	150	530	140	520
Soil 2.5	5.0	180	650	210	760
Soil 3.3	5.0	160	600	230	850
Soil 4.1	5.0	300	1100	240	870
Alum Shale	5.0	170	600	100	370
IAEA-135	1.0	6.8	25	7.3	27

As seen from table 11 the concentration of ^{226}Ra was 150 µg/kg in samples from Orrefjell (O1-O3) when corrected with ISTD, whereas it ranged from 130 to 160 µg/kg when corrected with yield. These samples were parallels of the same sample, and the average concentration of ^{226}Ra corrected with ISTD and yield was respectively 150 ± 0.0µg/kg and 140 ± 15µg/kg. The measurement, and precision, of the parallels were considered good with results within a small range. The concentrations corrected with ISTD and yield, were close, which was considered as a good results.

The soil samples from Schöpke had different amounts of alum shale mixed in the soil (Shcöpke, C. 2017). Sample 2.5 has no alum shale mixed in, whereas soil sample 3.3 and 4.1 has respectively 5% and 25% alum shale mixed in the soil. Sample 2.5 had concentration 180 µg ^{226}Ra per kg, soil sample 3.3 and 4.1 had 160 and 300 µg ^{226}Ra per kg when corrected with ISTD. Correction with yield gave 210, 230 and 240 µg ^{226}Ra per kg for soil 2.5, 3.3 and 4.1, respectively. The corrections with yield gave a higher concentration-value compared to the correction with ISTD for soil sample 2.5 and 3.3. Soil sample 4.1 had a concentration of 300 µg ^{226}Ra per kg when corrected with ISTD compared to 240 µg ^{226}Ra per kg when corrected with yield. The alum Shale-sample had a concentration of 170 µg ^{226}Ra per kg soil when corrected with ISTD, and 100 µg ^{226}Ra per kg when corrected with yield. However, the samples from Schöpke´s, 2017, project were also measured by NRPA in Tromsø by Ge-detector, and the results from the two measurement techniques will be discussed in chapter *5.3.3.3 Comparison of Measurement on ICP-MS and Measurement by Ge-detector*. By comparing these results it was possible to verify the results and determine which of the correction techniques that was most accurate.

The certified reference material IAEA-135 had a 95% confidence interval between 21 Bq/kg to 25 Bq/kg. As seen from table 11 the correction with ISTD gave a concentration of 25 Bq ^{226}Ra per kg (6.8 µg/kg), and correction with yield gave 27 Bq ^{226}Ra per kg. By looking at the range given in the IAEA-135´s certificate, the most accurate results was obtained by correcting the results with ISTD. However, the results were in the higher range of the 95% confidence interval for the reference material.

5.3.3.3 Comparison of Measurement on ICP-QQQQ and Measurement by Ge-detector

As presented in chapter *5.3.3.2 Soil Samples*, the corrections with the two correction techniques gave different concentrations of ^{226}Ra in µg/kg soil. It was assumed that the concentration of soil sample 4.1 would be higher compared to soil sample 2.5 and 3.3, due to an increase of alum shale mixed in the sample. Since the concentrations of the soil samples were not known prior to measurement, it was not possible to determine which of the correction techniques were the most accurate just by looking at the results presented in table 12.

NRPA in Tromsø performed a measurement of three soil samples using gamma spectrometry – Ge-detector system (Mauring, A. 2015). The ICP-MS results for sample 2.5, 3.3 and 4.1 were compared with the measurement performed by NRPA Tromsø to verify the results. The comparison was performed with concentrations in Bq/kg. The results from the Ge-measurement can be found in table *D6*, attachment *5.3 Soil Samples*.

Table 12 shows the results from Ge- and ICP-QQQ-measurement; corrected with ISTD and yield.

Table 12. Concentration of ^{226}Ra, Bg/kg, measured by Ge-detector and ICP-QQQ (corrected with ISTD and yield). All concentrations from ICP-MS measurement is given with two significant figures.

Sample	Ge [Bq/kg]	ISTD [Bg/kg]	Yield [Bg/kg]
Soil 2.5	670 ± 14	650	760
Soil 3.3	790 ± 17	600	850
Soil 4.1	1000 ± 21	1100	870

Figure 12 illustrates the difference between the concentrations measured on Ge-detector and ICP-QQQ.

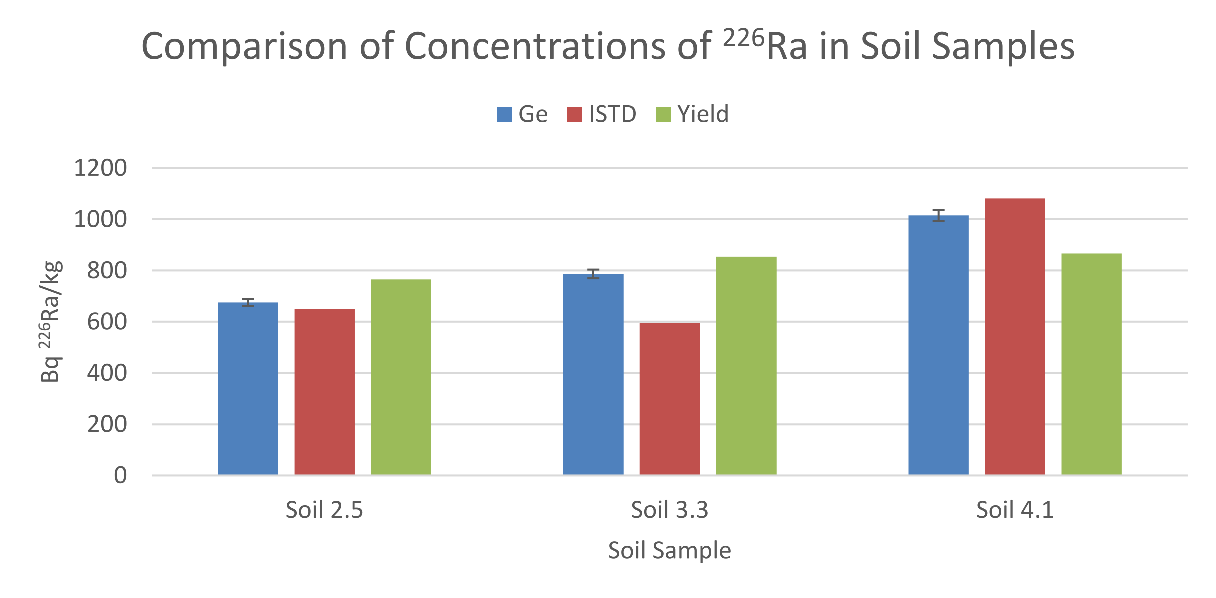


Figure 12. Comparison of concentrations in Bq/kg measured by Ge-detector and ICP-MS. Corrections with ISTD or yield represents measurement by ICP-MS. Data can be found in table 13.

By looking at figure 12, it looks like the three measurements corresponded. The correction with ISTD underestimated the concentration of ^{226}Ra for soil sample 2.5 and 3.3, but overestimated the concentration for soil sample 4.1 when comparing the results to Ge-results. The correction with yield overestimated the concentration of ^{226}Ra in soil sample 2.5 and 3.3 compared to Ge-measurement, and underestimated the concentration in soil sample 4.1.

As mentioned it was assumed that an increase of alum shale mixed in the sample, would increase the concentration of ^{226}Ra. The results from Ge-measurement shows an increasing concentration with increasing amounts of alum shale, whereas this was not the case for ICP-MS-measurement when correcting with ISTD. ISTD-correction gave a lower concentration of ^{226}Ra in soil sample 3.3 (5% alum shale) compared to soil sample 2.5 (0% alum shale). Correction with yield gave a higher concentration in soil sample 4.1 (25% alum shale) compared to soil sample 3.3 (5% alum shale), but not a huge difference compared to Ge-measurement which gave an increase of 228 Bq/kg from soil sample 3.3 to 4.1.

To verify whether there was a significance difference between ICP-MS measurement and Ge-measurement, a statistical test was performed using Minitab 16. A One-Way ANOVA test was performed with a null hypothesis stating equal populations means in the three groups. The alternative hypothesis was that at least one of the means were different. The One-Way ANOVA data output can be found in attachment *7.1 One-Way ANOVA: Comparison of ICP-QQQ and Ge-Detector Schöpke, C. 2017*. The p-value given in the output is 0.927 which indicates that there was not enough evidence against H_0. Thus, the hypothesis assuming equal population means cannot be rejected. As seen from the output, the results from the Ge-measurement did not significantly differ from measurement on ICP-QQQ (both yield- and ISTD-corrected). As seen from the data output, the 95% confidence intervals overlap, indicating again not enough evidence against the null hypothesis with *these* data.

It is important to point out the number of measurements performed in this thesis. An aspect of the test which is important to consider is parallels. Only one sample for each soil type was prepared using the procedure presented in this thesis. More parallels should have been prepared and measured to get an idea of the precision. Several parallels should also have been prepared and measured by ICP-MS to obtain a more reliable result for all soil samples. Since only one parallel was measured per soil sample, there was a chance that these samples were not the most representative for the soil sample, thus affecting the comparison of the measurement techniques. The accuracy of the results, for both yield- and ISTD-corrected, were good compared to Ge-detector by looking at the results of the One-Way ANOVA test performed.

5.3.3.4 Interferences – Matrix Effects

Both soil-, produced- and formation water samples have complex matrices, and as presented in chapter *3.3.3.1 Interferences – Matrix Effects*, it was desirable to obtain an idea of which other elements that might be present in the samples in addition to ^{226}Ra. As mentioned in the previous chapters concerning recovery measured on NaI, the yield recovery ranged from 14-61% for water samples, and 5% to 88% for soil samples, making it interesting to check whether some elements were affecting the yield recovery. The results presented in this chapter are only estimates. The concentrations of these elements were not known, and the loss of these elements during sample preparation cannot be quantified. This uncertainty is important to keep in mind when evaluating the data.

As seen from the results presented in attachment *6 Which Elements are Present in the Samples,* table *E2* and *E3*, there were relatively high concentrations of some rare earth elements in both water samples and soil samples. For example, the concentration of europium ranges from 160-180 µg/L in produced water samples. The produced water samples have a concentration of lanthanum ranging from 49-62 µg/L. The produced water samples has a high concentrations of strontium, Sr; ranging from 1.2-1.5 g/L. Strontium is one of the interferences which was supposed to be washed out during the ion exchange-separation. There were also high concentrations of barium in the samples: 7.4-7.8 g/L. It is possible that equilibrium has occurred between stable barium and the isotope ^{133}Ba, but this is just an assumption.

The concentrations of rare earth elements range from µg/L to several mg/L, from 1.3 µg Hf/L to 18 mg Ce/L. The concentrations of rare earth elements are higher in soil samples compared to the water samples. The concentration of europium in soil samples, 2.5, 3.3, 4.1 and alum shale, ranged from 270 µg/L to 390 µg/L. The high concentrations of rare earth elements corresponded well with the digestion technique – the recovery of rare earth elements were great after digestion with H_3PO_4 on UC for 40 minutes, 260°C, as discussed in chapter *5.1.3.1 Digestion of Rare Earth Elements (REE).*

Soil sample 4.1 and alum shale have high concentrations of aluminum; 5,1 and 5,2 g/L. The samples, including the certified reference material IAEA-135, had a deep orange/brown color, which can be explained by the high concentrations of iron: 0.34-1.5 g/L Fe. There are also relatively high concentrations of magnesium in these three samples, 58-240 mg/L Mg.

Another theory discussed was the possibility of particle adsorption of ^{133}Ba. Conditions such as pH and presence of metal oxides (e.g., oxides of aluminum, manganese and titanium) can affect the partitioning of barium in the environment. According to Agency for Toxic Substances and Disease Registry, ATSDR, high cation exchange capacity in fine textured mineral soils or soil with high organic matter content, can affect the mobility of barium. The mobility will be affected by adsorption. Barium can react with hydroxides and metal oxides in soil can be adsorbed onto soil particulates ATSDR).

By directly looking at the results, it was not possible to see a pattern – whether some elements affected the yield. The concentrations of other elements varied a lot, and the recovery varied a lot. Therefore a chemometric analysis was performed. According to Bu, D. PhD, Principal Scientist at CAMO Software Inc., chemometrics is:

> “*Chemometrics is the use of mathematical and statistical methods to improve the understanding of chemical information and to correlate quality parameters or physical properties to analytical instrument data. Patterns in the data are modeled; these models can then be routinely applied to future data in order to predict the same quality parameters.”*
> *Bridging the Gap Between the State and Measurement of a Chemical System for Chemometric*,
> Bu, D. PhD, Principal Scientist at CAMO Software Inc. *Analysis for Spectroscopy*

Multivariate statistics refers to the collection of tools available to analyze three or more variables at the time. With multivariate analysis it is possible to detect patterns between the variables. PCA, Principal Components Analysis, is not a test of significance and no null hypothesis is required. However, PCA should be followed by further investigation of the data; generate a hypothesis about what the ordination diagram is showing (Shaw, P. J.A. 2003).

Figure 13 shows the results from the PCA-test performed in the statistics program JMP. A biplot was made, which illustrates the correlation of elements, yield and sample type. Sample information can be found in attachment *6 “Which Elements are Presents in the Samples?”,* table *E4*, and the information was used to make the PCA-test illustrated in figure 13:

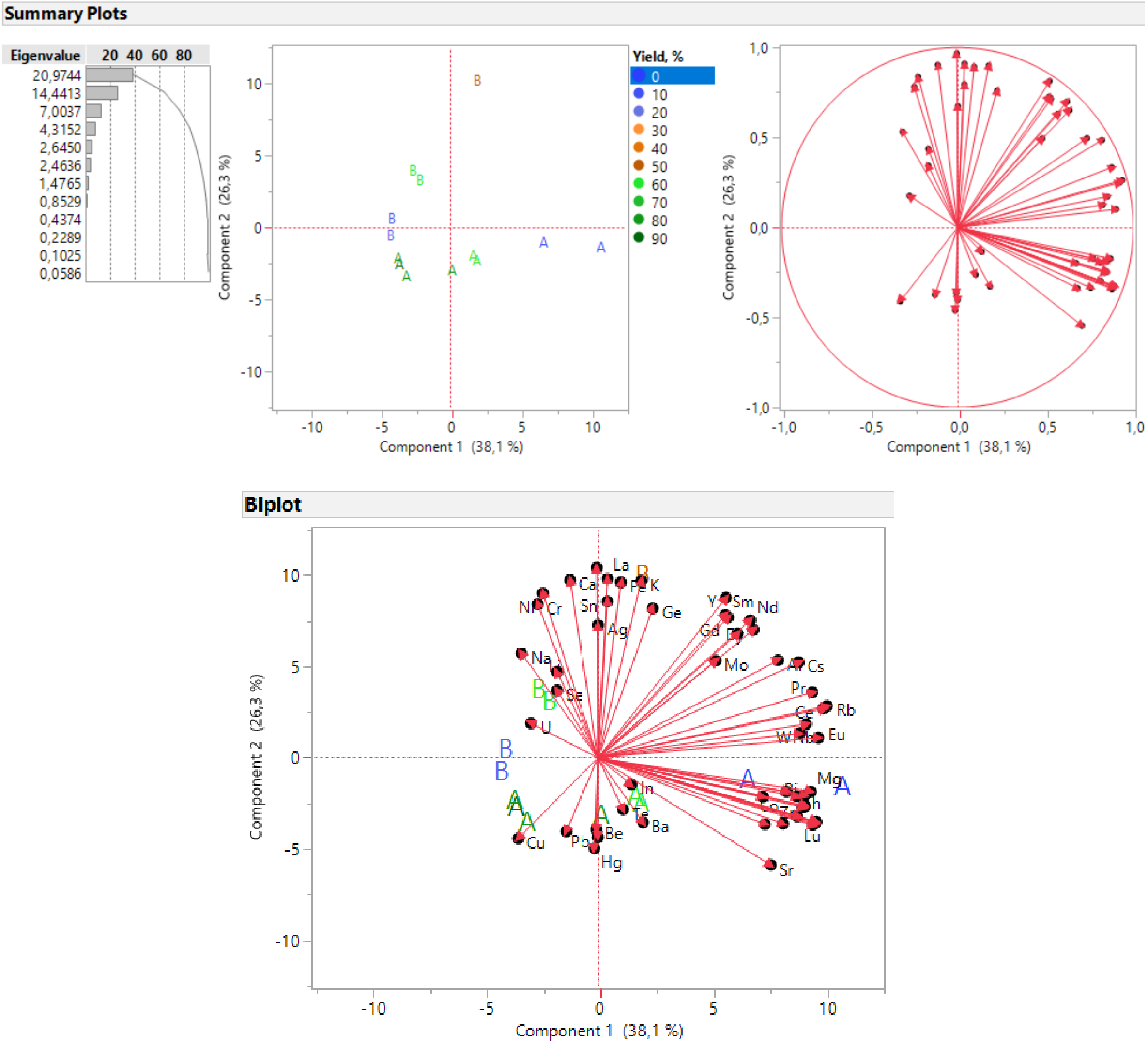


Figure 13. Results from PCA-test performed in JMP. The test is performed for both soil(A) and water (B). Sample information can be found in table *D4*, and data can be found in table *E2* and *E3*, attachment *6 Which elements are present in the samples?*

Figure 13 illustrates the correlation between elements, sample type and yield. As seen from the summary plots, soil(A) and water(B) differed in correlation with elements.

The water samples with high yields, illustrated with a green B, had a correlation with Se, Na and Li. These are the produced water samples fractionated >0.45 µm and >10 kDa. The concentration of Na was great in both samples. However, >10 kDa has 56 mg/L Na and >0,45 µm had a concentration of 14 mg/L Na. The produced water sample (total) with a medium recovery, orange B, was affected by La, Fe, K. The greatest correlation seems to be with K. The two formation water samples, K1 and K2, are illustrated by a blue B, which indicates low yield for water samples. According to the PCA-test, it was not clear which element that could have affected the low yield. However, by looking at the figure, it can look like uranium have affected the yield. The concentration of uranium in these two samples were much greater, 12-14 µg/L, compared to all the other samples – both water and soil samples. As it looks, it was assumed that high concentrations of uranium in water samples can affect the behavior and recovery of ^{133}Ba.

The three soil samples from Orrefjell, O1-O3, are illustrated with dark green A, since the yield was high. The figure illustrates a high concentration of Cu in these samples. However, since these samples had a good yield, measured on NaI, it was assumed that ^{133}Ba's behavior would not be affected by this element. Soil sample 2.5 and 3.3, from Christian Schöpke's master project, have medium recovery of ^{133}Ba, and are illustrated with an A in light green. These samples had a correlation with Ba, Te and In according to the results of the PCA-test. A high concentration of Ba could create an equilibrium-effect in the column, and affecting the recovery of ^{133}Ba. The certified reference material, IAEA-135, is also illustrated with a dark green A, indicating a high recovery. The CRM had a correlation with Be, As, Hg and Pb. The two samples, 4.1 and alum shale, had low recovery and are illustrated with the letter A in a dark blue color. As seen from the figure, these were different from the Orrefjell samples O1-O3 (component 1). These two samples seem to have a correlation with the following elements; Bi, Mg, Cd and Mn. Other elements are also pointing the direction of these samples, like Zr, Tb, Tm, Er, Th, Ti, Sb, Ho and Ta. Thus, the high concentrations of Fe and Al do not seem to affect the recovery of ^{133}Ba in these two samples.

As mentioned in this chapter, PCA is not a test of significance and no null hypothesis is required, and should be followed by further investigation of the data. However, due to time limitations no further laboratory work was performed to test whether or not the elements in correlation had an effect on the yield.

As seen from the PCA-test, figure 13, the recovery of ^{133}Ba seems to be affected differently according to sample type. However, it is not known whether ^{226}Ra is affected by these elements – the relationship between ^{133}Ba and ^{226}Ra will be discussed further in chapter *5.4.3 ^{133}Ba as Yield Monitor and Internal Standard*.

5.4 Quality Assurance and Statistics

5.4.1 Blanks

^{226}Ra was present in all upconcentrated blank samples, and in soil blank 1 the concentration was 16 pg ^{226}Ra/L with a relative standard deviation of 10%. The other blank samples also contained ^{226}Ra, which can indicate contamination during sample preparation. Ideally, the blank should contain as little or no analyte to obtain a low detection limit. Soil blank 4 had an concentration of 9.1 pg/L ^{226}Ra compared to 5.6 pg/L ^{226}Ra and 5.9 pg/L ^{226}Ra in soil blank 2 and 3, respectively. All blank samples, except soil blank 1, had a high relative standard deviation; 37-56%. To check whether or not Soil Blank 1 is an outlier, Grubbs' test was performed with the following results;

Table 13. Results from Grubbs' test - Outliers. The test has been performed with concentrations in upconcentrated samples, 8 mL. Data can be found in attachment *5 Determination of ^{226}Ra in Unknown Environmental Samples,* table *D1*.

Mean	8.520
SD	4.417
# of values	5
# of rows w/o data	1
Outliers detected?	No
Significance level	0.05 (two-sided)
Critical Value of Z	1.7150364677

Row	Value	Z	Significant Outlier?
1	6.0	0.571	
2	16.0	1.694	Furthest from the rest, but not a significant outlier (P > 0.05)
3	5.9	0.593	
4	5.6	0.661	
5	9.1	0.131	

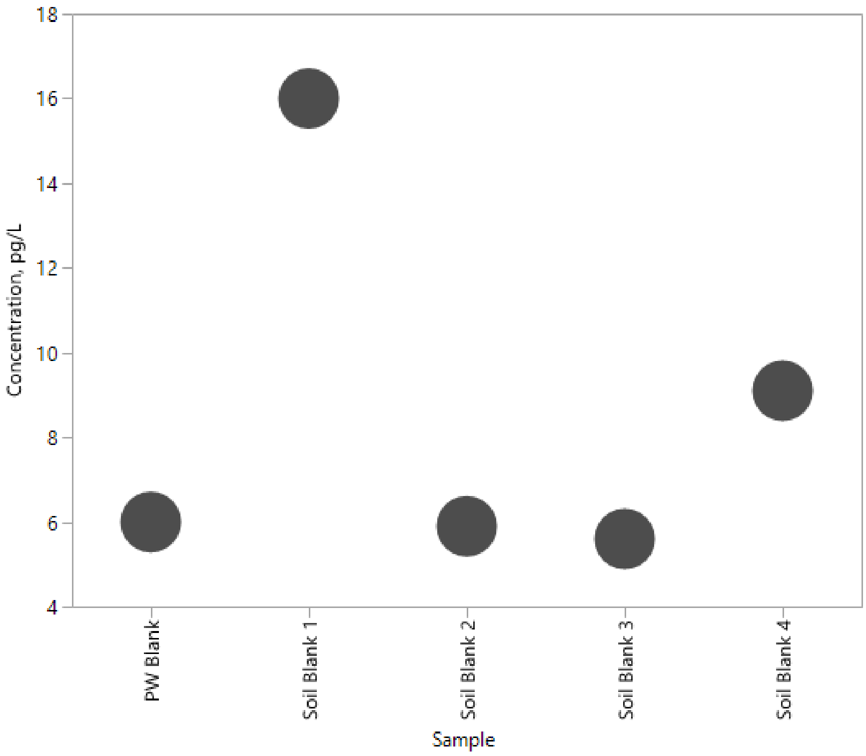


Figure 14. Bubble Plot of Concentration, pg/L ^{226}Ra, in upconcentrated Blanks. Data can be found in attachment *5 Determination of ^{226}Ra in Unknown Environmental Samples,* table *D1.*

According to the test results, displayed in table 13, Soil Blank 1 was not an outlier and should therefore be included in the calculation of LOD and LOQ. The detection limit reported in chapter *5.3.2 Limit of Detection and Limit of Quantification*, was 0.020 pg/L ^{226}Ra for water procedure and 7.8 pg/kg for soil procedure. By including the Soil Blank 1, the detection limit and quantification limit for ^{226}Ra and ^{228}Ra are presented in table 14;

Table 14. Limit of Detection and Limit of Quantification for water- and soil procedure.

	^{226}Ra → ^{242}Ra pg/L	^{226}Ra → ^{242}Ra [pg/kg]	^{228}Ra → ^{244}Ra pg/L	^{228}Ra → ^{244}Ra [pg/kg]
LOD:	0.052	21	0.0008	0.3
LOQ	0.17	69	0.003	1

By comparing the two LOD-values, it is clear that Soil Blank 1 had an great effect on the limit of detection. Considering the results of the outlier test, the limit of detection for this project should be 0.052 pg/L ^{226}Ra for water procedure, not 0.020 pg/L ^{226}Ra as reported in chapter *5.3.2 Limit of Detection and Limit of Quantification*. However, both reported LOD-values are below the compared the required upper limit set by USEPA – 1 pg/L ^{226}Ra for analytical methods used for analyzing drinking water (Park, C. J. et al. 1998).

The limit of detection should be 21 pg/kg for soil procedure, and not 7.8 pg/kg as reported in *5.3.2 Limit of Detection and Limit of Quantification*. It was assumed that the UC-vials had been contaminated prior to use, since the same vials previously have been used for digestion of soil samples possibly containing ^{226}Ra.

5.4.2 Precision and Accuracy

As seen from table 11 in chapter *5.3.3.1 Water Samples*, the concentration of ^{226}Ra ranged from 0.083 to 0.37 pg/L in samples from Orrefjell when corrected with ISTD, whereas it ranged from 0.063 to 0.28 pg/L when corrected with yield. The concentrations corrected with yield were consistently lower in all samples compared to concentrations corrected with ISTD. When evaluating the accuracy of the method, both Orrefjell water samples and spiked water samples were evaluated. The precision of the method could not be evaluated, since there were no parallels.

Table 15 displays the measurement of spiked samples and Orrefjell 1-4 from two times of measurements. The table also shows the suppose-to-be concentration range for ^{226}Ra in the spiked samples.

Table 15. Concentration of ^{226}Ra in pg/L and Bq/L for water samples measured two times on ICP-MS. First measurement was in November 2016 during optimization of measurement, whereas second measurement was in March 2017. Significance figures: 2.

		NOVEMBER		MARCH	
Sample Name	**Suppose-to-be Concentration [pg ^{226}Ra/L]**	**Yield [pg ^{226}Ra/L]**	**ISTD [pg ^{226}Ra/L]**	**Yield [pg ^{226}Ra/L]**	**ISTD [pg ^{226}Ra/L]**
0.001Bq/L	0.027	0.030	0.035	0.039	0.048
0.01Bq/L	0.27	0.23	0.31	0.25	0.32
0.1Bq/L	2.7	1.9	2.9	2.6	3.2
Orrefjell 1	-	0.099	0.15	0.12	0.14
Orrefjell 2	-	0.084	0.14	0.12	0.14
Orrefjell 3	-	0.17	0.34	0.26	0.34
Orrefjell 4	-	0.051	0.090	0.063	0.083

The samples were measured at two different times to check the repeatability of the instrument's measurement. Table 15 shows a higher concentration in pg/L for the second measurement (March). This applies for both yield corrected concentrations and ISTD corrected concentrations.

As seen in table 15 the accuracy varied for all samples regardless of the correction technique and time of measurement. The spiked sample 0.001Bq/L concentrations, with a known concentration of 0.027pg ^{226}Ra/L, were higher than the suppose-to-be concentration in both November and March regardless if it was corrected with yield or ISTD. The corrections with ISTD gave higher concentrations compared to yield corrected concentrations. It was assumed that the second measurement would give more accurate results since during the optimization and analysis performed in November, since two gas modes were used – no gas and N_2O. As mentioned in previous chapters, this could cause drift in the instrument. The results from both November and March were drift corrected, but using only nitrous oxide as gas mode, it was assumed that the changes in the instrument's reading over time would decrease – giving more accurate results for both ^{133}Ba and analyte, ^{226}Ra.

A statistical test was performed to check for significance difference between the two correction-techniques. The test performed was One-Way ANOVA, and the software used was Minitab 16. The null hypothesis assumed equal group means. Ideally the mean values for these four "groups" should be equal, since it is the same samples that were measured. The groups were divided into time of measurement (November or March) and correction-technique (yield or ISTD), as presented in table 27. The test gave a output found in attachment *7.2 One-Way ANOVA: Comparison of Yield- and ISTD corrections in Spiked Samples (November/March)*. The One-Way ANOVA test gave a p-value of 0.996, which is greater than 0.05. Thus, the null hypothesis could not be rejected, indicating no significance difference between the group means. According to the results, it was concluded that the repeatability of the measurements were good due to no significance difference between the group means in terms of measurement time.

A One-Way ANOVA with a Tukey-test was performed for groups "Initial Conc. pg/L" "pg/L Yield March", and "pg/L ISTD March", and it gave the output presented in attachment *7.3 One-Way ANOVA: Comparison of Yield- and ISTD corrections in Spiked Samples (March)*. The Tukey tests indicated that there was no significance difference whether the correction was performed with yield or ISTD. The p-value was 0.982, which indicated poor evidence to reject the null hypothesis stating equal group mean values. It is important to state that the number of samples were three (N = 3), so the results should be evaluated accordingly. With only three samples, the results of the test cannot be fully trusted. More samples and parallels should have been measured to gain certainty in the data output – this applies for all statistical tests presented in this thesis. As the statistical test stated there was no significance difference in the concentrations corrected with either yield or ISTD. Thus, measurement of ^{226}Ra could be corrected with either ^{133}Ba as yield or ISTD according to these results – both giving accurate results for freshwater samples.

The accuracy of the method for more complex water samples were considered ok. The formation water, LRM, from Poland had been estimated to be 100 ± 26 pg ^{226}Ra/L ^{226}Ra (3.7 ± 0.95 Bq/L). Ten results of ^{226}Ra concentration had been reported, and the results varied from 55 to 131 pg ^{226}Ra/L ^{226}Ra (2.0 Bq/L to 4.8 Bq/L) (Bonczyk, M., Michalik, B. 2016). The results from the procedure presented in this thesis, gave results ranging from 110 to 160 pg ^{226}Ra/L depending on which correction technique that was used. The results were in the higher range of the results, and further development of the procedure can perhaps give more accurate and reliable results. The precision of the samples was not determined, since only two samples were measured.

The concentration of ^{226}Ra in soil from Orrefjell had been measured by NRPA Tromsø, and was determined to be 550 ± 15 Bq ^{226}Ra/kg with two significance figures. The soil samples from Orrefjell (O1-O3) had an average concentration of 530 ± 0.0 Bq/kg corrected with ISTD, and 520 ± 42 Bq/kg corrected with yield, and 570 ± 60 Bq/kg when not corrected with either ISTD or yield. A One-Way ANOVA test was performed using Minitab 16 to check for significance differences in group means, which ideally should be equal. The null hypothesis was equal group means, and alternative hypothesis was that one or more groups means differed from the others. The comparison was performed with concentrations in Bq/kg. The One-Way ANOVA gave the output presented in attachment *7.4 One-Way ANOVA: Comparison of ICP-QQQ (yield/ISTD) and Ge-detector for Orrefjell Parallel Samples (O1-O3)*. The output shows a p-value of 0.387, indicated that there not enough evidence to state that the group means were significantly different from each other. Thus, the null hypothesis cannot be rejected. This was desirable, since it indicated that there was no significant difference between the measured value from NRPA Tromsø and the measured value from the ICP-QQQ. The concentration of ^{226}Ra ranged from 481 to 565 Bq/kg when corrected with yield. The mean value closest to the reference-mean value was correction with ISTD; 530 ± 0.0 Bq/kg compared to 550 ± 15 Bq/kg – thus, assuming best accuracy and precision when correcting the results with ISTD. However, more tests should be performed before claiming that the newly developed procedure gives as precise and accurate results as already existing procedures, like Ge-measurement and coprecipitation with $BaSO_4$ before measurement on α-spectrometer.

As discussed in chapter *5.3.3.3 Comparison of Measurement on ICP-QQQ and Measurement by Ge-detector*, the population means of the ICP-MS-results were not significantly different compared to Ge-results from Schöpke, C. (2017) – p-value of 0.927. The accuracy of the ICP-MS results were therefore considered relatively good. The precision of the results could not be determined, since no parallels were prepared – only one measurement of each sample.

There was no significance difference between correction with ^{133}Ba as ISTD or yield, thus, both correction techniques can be applied for samples with little or no matrix and samples with high matrix. The repeatability was also considered to be good for spiked water samples. According to the results given in this master thesis, the procedure can provide accurate results for both samples with little or no matrix and samples with high matrix.

5.4.3 ^{133}Ba as Yield Monitor and Internal Standard

The results for ^{226}Ra presented in the previous chapters were corrected either with ^{133}Ba as a yield or as an internal standard. The yield was measured on NaI-detector, and the recovery of the internal standard was measured directly on ICP-QQQ. As discussed in chapter *5.4.2 Precision and Accuracy*, there was no significance difference between yield- and ISTD-corrected results.

A test to check whether or not ^{133}Ba was a good yield monitor and internal standard for ^{226}Ra was performed. The ratio, counts per second, between ^{226}Ra and ^{133}Ba in the two solutions was calculated to be 0.43 and 0.33 respectively for sample solution and reference solution. Prior to the test, it was assumed that an equal ratio between the two solutions would indicate that ^{133}Ba was a good yield monitor and internal standard for ^{226}Ra. If the ratios were different from each other, this would indicate that ^{133}Ba does not behave similar to ^{226}Ra – thus, not being a good yield monitor and internal standard for ^{226}Ra. As mentioned, the ratios were not equal. This indicates that ^{133}Ba and ^{226}Ra do not behave similar, chemically. The sample solution had a greater ratio of ^{226}Ra compared to the reference solution, as shown in figure 15.

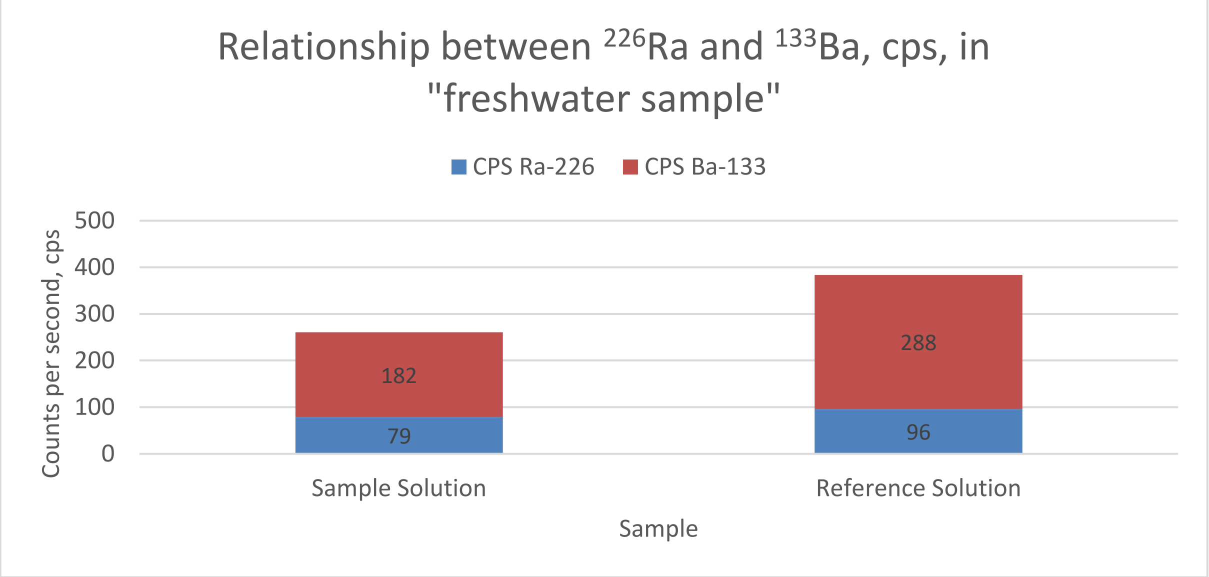


Figure 15. Relationship between ^{226}Ra and ^{133}Ba, counts per minute. The relationship in reference solution was calculated to be 33%, whereas in sample solution it was calculated to be 43%.

According to these results, it was assumed that ^{226}Ra has a greater affinity to the resin material compared to ^{133}Ba. The ratio between ^{226}Ra and ^{133}Ba changed through the sample preparation. This would affect the calculated concentrations of ^{226}Ra in unknown samples, since the concentrations were corrected with the loss of ^{133}Ba. As mentioned, all quantifications of ^{226}Ra were corrected either with ^{133}B a as yield or internal standard. Thus, a systematic error was present in all quantifications of ^{226}Ra when using ^{133}Ba to correct for loss of analyte. The systematic error has not been corrected for in the results presented in the previous chapters. However, this systematic error is an important aspect of the sample preparation to consider in further analysis due to the effect on quantification of analyte.

The test was performed with water containing little or no matrix, illustrating the relationship between ^{226}Ra and ^{133}Ba in freshwater samples. As discussed in previous chapters, there were relatively high concentrations of rare earth elements and other elements like Fe and Al in some of the high matrix samples. The high concentrations of other elements might influence ^{133}Ba´s affinity to the resin, making it easier to elute from the resin compared to ^{226}Ra. Due to a change in samples containing little matrix, it is assumed that the relationship is even more affected when working with samples like produced water and soil. However, according to the PCA-test discussed in chapter *5.3.3.4 Interferences – Matrix Effects*, it seemed like the recovery of ^{133}Ba, measured on NaI, correlated with different elements according to sample type.

The rare earth elements have a higher mass compared to ^{133}Ba: ^{135}La to ^{175}Lu. Space charge effects within the ICP-QQQ might explain some part of the low yield recovery in the soil samples. Space charge effects are a consequence of mutual repulsion between particles of like charge (Busch, Ken 2004). ^{133}Ba has a smaller mass compared to ^{226}Ra and some of the rare earth elements, which may cause space charge effects affecting the ratio between ^{226}Ra and ^{133}Ba. However, this is an assumption that needs to be tested further.

5.5 Errors and Further Development of the Procedure

In previous chapters, several errors and assumed errors were presented. Some of the most relevant errors will be presented again in this chapter, and be discussed in the view of the full procedure and further development of the procedure to obtain better results.

The first aspect concerning errors and further need of investigation is the precision and accuracy of the method. There were no parallels, except for soil samples from Orrefjell (O1-O3), which makes it impossible to determine the precision of the procedure and measurement. Parallel samples are necessary to determine the precision of the measurements. The precision of the Orrefjell soil samples were considered to be good since the results were within a small concentration range: correction with ISTD. The precision was variable when correcting with yield.

The accuracy was possible to determine by comparing the results of the ICP-MS with the results of another independent method. The comparisons between Ge-measurement and ICP-QQQ showed that there was no significant difference between the group means – indicating a good accuracy for the soil samples from Christian Schöpke's master project. The One-Way ANOVA test performed for spiked freshwater indicated no significance difference between the group means, thus, a good accuracy was assumed. The repeatability was also considered to be good for these results. However. the results varied, and the accuracy of the measurements can be improved – this will be discussed in chapter *5.5.1 ^{133}Ba as Yield monitor or Internal Standard – Is it a good choice?.*

5.5.1 ^{133}Ba as a Yield Monitor or Internal Standard – Is it a good choice?

An important systematic error to consider is the use of ^{133}Ba as a yield monitor and internal standard. The relationship between ^{226}Ra and ^{133}Ba should ideally be equal before and after sample preparation – however, this was not the case in this project. The results showed that prior to sample preparation the ratio was about 33%, and after sample preparation the ratio was 43% - the relationship changes through the sample preparation. Thus, this indicates that ^{226}Ra and ^{133}Ba did not behave chemically as similar as desired, which in turn affected the calculated amounts of ^{226}Ra. Therefore, the quantification of ^{226}Ra is not fully reliable when using ^{133}Ba to correct for loss or identify matrix problems for ^{226}Ra.

The test illustrated the relationship for freshwater samples, so it is assumed that the relationship is even more changed when working with samples like produced water and soil. According to these results, it is assumed that ^{226}Ra has a stronger affinity to the resin compared to ^{133}Ba. It is important to point out that only one test was performed, so to validate these results further testing should be done. This systematic error is an important aspect of the sample preparation to consider.

As discussed in *5.4.2 Precision and Accuracy*, there was no significant difference according to the One-Way ANOVA test between spiked water samples' suppose-to-be concentration and yield- and ISTD-corrections. There was no significance difference for soil samples either. However, the results varied between the soil samples and correction technique, perhaps this can be explained by the changing relationship between ^{133}Ba and ^{226}Ra. No significance difference between the group means and suppose-to-be concentrations, indicates accurate results for both soil and water samples. However, the accuracy can be improved, and be evaluated with the changing relationship in mind. It is important to point out that only one test was performed, so to validate these results further testing should be done. However, the results obtained in this master project show that ^{133}Ba can be used as internal standard and yield.

It would have been desirable to test ^{228}Ra as a yield monitor/internal standard for ^{226}Ra. ^{228}Ra is an isotope of Ra, which means that ^{228}Ra and ^{226}Ra probably will behave chemically more similar than ^{133}Ba and ^{226}Ra. ^{228}Ra has a half-life of 5.7 ± 0.040 years, and decays 100% by beat minus particle emission (NIST. 2016). Thus, in this scenario yield determinations cannot be performed by using NaI-detector since ^{228}Ra do not decay by gamma emission (NIST, 2016). In other words, ^{228}Ra will act as an internal standard measured directly on ICP-MS; documenting the loss and effects throughout the whole procedure from sample preparation to measurement of ICP-MS. ^{228}Ra was used a yield monitor to determine the yield recovery in a study performed by Larivière D. et al from 2006. According to NIST, National Institute of Standards and Technology, ^{228}Ra is mainly used as yield monitor in quality assessment of water supplies, but has also been used to estimate the age of radiobarite-formations in scale and sludge deposits from oil production. However, ^{228}Ra is found naturally in environmental samples, so it is important to add a concentration of ^{228}Ra-ISTD a in such an extent that the natural abundance of ^{228}Ra is neglected. Due to time limitations, no further testing with either ^{133}Ba or ^{228}Ra was done during this master project.

5.5.2 Recovery through Ion Exchange-Separation

Park et al. published an article in 1998 where ^{226}Ra in water samples was determined using HR-ICP-MS after cation exchange as sample preparation. . The article does not mention any use of ^{133}Ba or any other element as yield monitor, or internal standard. Park et al. reported a recovery efficiency better than 97% and matrix separation efficiency higher than 99% for calcium. However, the procedure was only applicable to mineral water samples, and a recovery efficiency at 22% for seawater was reported (soil samples were not measured in this study) (Park et al. 1998).

Matrix problems were a part of this procedure. There were several other elements present in soil samples, probably interfering with the separation on the column. Good resolution and a long column life requires a sample being relatively free from particulate matter (Pharmacia Biotech). The average recovery efficiency of the procedure presented in this master thesis was 81 ± 6.4% and 57 ± 5.3% respectively for freshwater and produced water. The average recovery efficiency for soil samples was 62 ± 36% if soil sample 4.1 and alum shale were included, whereas if these two soil samples were excluded the average recovery efficiency was 81 ± 11%. Hence, if this procedure is to be used, it is expected a lower yield recovery of ^{133}Ba if the conductivity of the sample is high, e.g. produced water. If a higher yield recovery is desirable, the procedure for sample preparation must be optimized further.

There were steps during the separation where ^{133}Ba was eluted from the column. The most critical steps in the ion exchange-separation were elution of calcium, magnesium and strontium with ammonium acetate and the washing step with 3M hydrochloric acid. The average presence of ^{133}Ba combined found in these steps were 5.8 ± 2.5% and 8.7 ± 4.3% for, respectively, freshwater samples and produced water. For soil the average presence of ^{133}Ba was 3.4 ± 4.4%, including the two samples containing high amounts of alum shale. Thus, these were critical steps for all matrices tested in this thesis.

An assumption was that there are other elements with greater affinity to the resin compared to ^{133}Ba. In other words, the cation resin is saturated with other elements, making ^{133}Ba elute earlier than desired. As the ^{226}Ra/^{133}Ba-test showed, it seemed like ^{226}Ra had a greater affinity to the resin than ^{133}Ba. This affected the quality of the separation, since ^{133}Ba behaved chemically different to the analyte. It is not possible to know whether or not these steps are critical for ^{226}Ra as well.

As presented in chapter *5.3.3.4 Interferences – Matrix Effects*, the produced water samples contained approximately 1.3 g/L strontium, 7.6 g/L barium and at most 0.15 g/L calcium. At most there was 5.9 mg/L magnesium in these three samples of produced water. The soil samples had an average concentration of 65 ± 100 mg/L magnesium, with 240 mg/L at most. The average concentrations of strontium and calcium in soil samples were 20 ± 9.3 mg/L and 0.41 ± 0.36 mg/L, respectively. It is not possible to determine whether the separation has been effective in terms of removing Sr, Ca and Mg since the concentrations of these elements were not known prior to measurement, and these concentrations were just estimates. The PCA-test performed showed the correlation between different elements, sample type and yield recovery. The plot showed that recovery of ^{133}Ba seemed to be affected differently according to sample type. However, it is not known whether ^{226}Ra was affected by these elements due changing relationship between ^{133}Ba and ^{226}Ra.

However, the PCA is not a test of significance and no null hypothesis is required, and should be followed by further investigation of the data. An interesting approach would be to add different concentrations of these elements to samples and check for correlation between behavior of ^{133}Ba and increasing concentration of the elements. However, due to time limitations no further laboratory work was performed to test whether or not the elements in correlation had an effect on the yield.

Another approach to improve the separation efficiency, is to use another resin material. The resin material used in this project was Bio-Rad AG 50W-X12. Larivière et al. used Bio-Rad AG 50W-X8 and Eichrom Sr-Spec resin for the pre-concentration and separation of ^{226}Ra in their study "*Determination of ^{226}Ra in Sediments by ICP-MS*". Larivière et al. reported a chemical yield of 83 ± 13% in their article, and an internal standard response, Rh, of 95 ± 2%. The detection limit was reported to be 0.006 pg/g (Larivière et al. 2003). The separation technique used by Larivière et al. is not the same as the one used in this thesis, but perhaps this is a better preparation-technique for soil and sediments compared to procedure used this project.

The separation efficiency is considered somewhat effective, but the separation can be optimized further to avoid loss of yield/ISTD and analyte. Thus, leading to a better recovery and more accurate results. However, it is important to keep in mind that ^{133}Ba and ^{226}Ra did not behave similarly during the sample preparation. A loss of ^{133}Ba cannot be directly linked to a loss of ^{226}Ra, and these results might be invalid since it is assumed that ^{226}Ra has a stronger affinity to the resin.

5.5.3 Limit of Detection – Blank Samples

Other aspects of the procedure are the criteria concerning blank values and the use of another independent method for verification of the results.

^{226}Ra was present in all blank samples, and in soil blank 1 the concentration was 16 pg ^{226}Ra/L with a relative standard deviation of 10%. The other blank samples also contained ^{226}Ra, which can indicate contamination during sample preparation. A proper clean-up after procedure is therefore desirable to develop. The limit of detection in this project was determined to be 0.052pg ^{226}Ra/L for water samples when including soil blank 1 (16 pg ^{226}Ra/L). It is important to point out the fact that LOD and LOQ for water samples was calculated using soil blanks, thus, adding one additional step to the procedure. Digestion is not a part of the procedure for water samples, thus, this detection limit and quantification limit illustrates the "worst case scenario". USEPA requires a limit of detection lower than 1 pg/L for analytical procedures when working with drinking water, so according the results this requirement was met. The limit of detection for soil procedure was 21 pg/kg, if soil blank 1 was included. It was believed that the contamination of blank samples originated from poor cleaning of UC-vials.

Another approach to lower the contamination of blank samples, is to be very careful with the equipment used; new equipment every time if they are used for other analysis, or equipment specifically used for the analysis of ^{226}Ra. It is believed that a proper cleaning procedure of the vials after digestion or careful use of equipment can affect the LOD and LOQ in a positive way.

5.5.4 Digestion of Soil Samples

The sample preparation of soil can also be optimized further, considering digestion of soil. The recovery of barium, and thus radium, can be tested further. The tests performed to find the optimal digestion technique for barium was performed once. To validate these results the digestion step should be performed and tested several times to make sure the technique is reliable. The technique gave recovery results around 100 percent with HNO_3 and H_3PO_4. The drawback of this technique is the PO_4^{2-} group present. This group can cause contamination in UC-vials and in the ICP-MS if not properly cleaned, and thereby cause interferences in other trace analysis for phosphorous. Therefore, a properly washing procedure of both vials and ICP-MS should be developed, as well as a procedure for which vials and ICP-MS should be used.

The average recovery of ^{133}Ba measured by NaI-detector prior to measurement on ICP-MS was 62 ± 36% when including the two samples containing high amounts of alum shale – 4.9% and 5.7% recovery detected in upconcentrated sample solution. A recovery can be expected to range from 26-99% according to these results. By excluding the two samples, the average was calculated to be 81 ± 11%. This is a much more representative picture for most soil samples prepared by the procedure presented in this master thesis when using ^{133}Ba as a yield monitor. However, more research is needed if samples containing high amounts of alum shale are to be measured with this method; approximately 92% of the yield monitor was lost.

As seen through the previous subchapters, there are several aspects of this procedure that can be developed further to obtain better results. It was also desirable to make this procedure applicable for biota samples, for example earth worms. Unfortunately there was not enough time to test the method on biota samples, so this could be an interesting aspect for further development.

6 Conclusion

The goal for this master project was to develop a method to determine the content of ^{226}Ra in environmental samples using ICP-MS. It was desirable that the method was applicable to various types of samples with different types of matrices, e.g. freshwater, produced water and soil. It was desired to avoid coprecipitation with $BaSO_4$ and fewer interferences, and being less time-consuming procedure if there is an urgent need for results. It was desirable to measure the samples using ICP-MS, measuring on mass-to-charge ratio instead of emitted radiation.

The optimized procedure included pH-adjustment, digestion of soil samples, cation exchange and upconcentration of the samples prior to measurement on ICP-QQQ. Coprecipitation with barium sulphate was avoided. The procedure was time-consuming, but not laborious due to automated instruments like the Gilson MINIPLUSS 3 Peristaltic pump.

Various types of environmental samples were prepared by the developed procedure. The samples had different matrices, and the environmental samples included freshwater from Orrefjell, produced water from Troll C (salinity of 4.8% (w/V)), and soil samples from Orrefjell. By testing different types of samples, it was possible to determine if the method was applicable to various types of matrices – which was desirable. ^{133}Ba was used as both yield monitor and internal standard, measured on NaI and ICP-MS.

It was desirable to obtain at least 70% recovery of ^{133}Ba, and thus, ^{226}Ra. The average recovery of ^{133}Ba was determined to be 81 ± 6.1% freshwater samples. Produced water samples had an average recovery of 57 ± 5.3%. Hence, the assumption was correct – a more complex matrix influenced the recovery of the yield monitor. The average recovery of ^{133}Ba in soil samples was 62 ± 36% if soil sample 4.1 and alum shale were included. These two samples had a recovery of 4.9% and 5.7% respectively for soil sample 4.1 and alum shale, which greatly affected the average value and standard deviation. If these two samples were excluded, the average recovery of ^{133}Ba was 81 ± 11%. The critical steps of the ion exchange-separation were 1.5M ammonium acetate and 3M hydrochloric acid for all environmental samples.

The blank samples for produced water and soil were measured, and used to determine the limit of detection for *both* water- and soil procedure. The limit of detection was determined to be 0.052 pg/L for water procedure, including by soil blanks – thus, this is the worst case scenario LOD for water procedure. The LOD for water procedure was below the upper limit set by USEPA – 1 pg ^{226}Ra/L for methods used for analysis of drinking water. The limit of detection for soil procedure was determined to be 21 pg ^{226}Ra/kg soil. However, it is believed with a proper clean-up procedure, the limit of detection will decrease for soil samples. The Ultraclave-vials used in this project, have earlier been used for soil samples possibly containing ^{226}Ra – this could have affected the blank values.

Using N_2O as reaction gas excluded interference from polyatomic masses for ^{226}Ra, and ^{133}Cs for ^{133}Ba. It is not a conventional gas mode, but the advantage of measuring the recovery of ^{133}Ba directly on ICP-QQQ compared to NaI-detector, was the possibility to detect matrix effects present within he ICP-QQQ. Thus, it was possible to determine the recovery of the ISTD for the full procedure – sample preparation to complete measurement on ICP-QQQ. Eliminating the measurement of the yield monitor on NaI-detector, makes the duration of complete analysis shorter – which is desirable if there is a need for urgent results.

The results from ICP-QQQ, using N_2O as reaction gas and S-lens, showed that the measurements were accurate for spiked water samples, assuming accurate results for other freshwater samples as well. Precision could not be determined since no parallel-samples were used. There was no significance difference between yield- and ISTD-correction of the results for freshwater. Thus, both correction-techniques can be used.

The soil samples were diluted and measured with X-lens on ICP-MS, and to verify the results, compared to soil samples measured by Ge-detector. The Ge- and ICP-MS-measurements (yield- and ISTD-corrected) were compared to determine whether or not the new procedure was applicable for soil samples. The comparison showed that there was no significance difference between the group means. The p-value given in the output was 0.927, indicating not enough evidence against H_0. Thus, the hypothesis assuming equal population could not be rejected with these data. The control samples, soil samples from Orrefjell (O1-O3), were not significantly different from the measured value on Ge-detector – 550 ± 15 Bq/kg compared to 530 ± 0.0 Bq/kg corrected with ISTD, and 520 ± 42 Bq/kg corrected with yield. This indicated that the results of soil samples can be corrected with ^{133}Ba both as yield and ISTD.

There are several aspects of the method that should be optimized further. The most important aspect is the choice of yield monitor or internal standard. ^{133}Ba was used in this master project, assuming equal loss of ^{133}Ba and ^{226}Ra. However, the result from the one test performed, showed that the relationship between ^{226}Ra and ^{133}Ba changed throughout the procedure – ^{226}Ra seemed to have stronger affinity to the resin. For freshwater samples the ratio changed from 33% to 43% during sample preparation, and it is assumed that the ratio is affected even more with more complex matrix. Perhaps another internal standard should be used – Larivière et al. published an article in 2005 were ^{228}Ra was used as yield monitor for soil- and sediment samples.

Measurement of ^{226}Ra on ICP-QQQ, as presented in this thesis, can be used for determination of ^{226}Ra in water samples and soil samples. However, the results presented in this thesis are not fully reliable due to a changing relationship between ^{133}Ba and ^{226}Ra, lack of parallels and a small sample number (N). The LOD did meet the required upper limit set by USEPA for drinking water analysis.

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Attachments

1 Instrument Parameters

1.1 Inductively Coupled Plasma Mass Spectrometer – ICP-QQQ

	S-lens	X-lens	Unit
ACQUISITION PARAMETERS			
Points per peak	3	1	Point
Replicates	5	5	
Sweeps/Replicate	100	100	
Integration time/Mass	7	7 (0,5 for 169Tm)	sec
Monitored Mass Pairs: Element Name (Q1 -> Q2)	133Ba (133 -> 149) 226Ra (226 -> 242) 228Ra (228 -> 244)	133Ba (133 -> 149) 169Tm (169 -> 185) 226Ra (226 -> 242) 228Ra (228 -> 244)	
SAMPLE INTRODUCTION			
Sample Introduction	Loop injection, 6 port valve	Loop injection, 6 port valve	
Loop Size	1.0	1.0	mL
Stabilize after Injection	33	33	sec
Carrier Solution	1 (Ultra-pure HNO_3)	1 (Ultra-pure HNO_3)	(V/V)%
PLASMA PARAMETERS			
RF Power	1550	1550	W
Sample Depth	8	8	mm
Nebulizer Gas	0.7	1.08	L/min
Nebulizer Pumo	0.1	0.1	rps
Pump Tubing	ID 1.02	ID 1.02	mm
Spray Chamber Temp	2	2	°C
Spray Chamber	Scott double pass, Quartz	Scott double pass, Quartz	
Nebulizer	Micromist	Micromist	
Makeup Gas	0.5	0	L/min

Lenses All the lenses are automatically tuned for measurement using ^{226}Ra at 10ng/L			
Installed Lens	S-lens	X-lens	
Cell			
N_2O Gas Flow Rate	0.3	0.3	mL/min
OctP Bias	-8	-8	V
OctP RF	200	200	V
Energy Discrimination	-7	-7	V
Wait Time Offset	2	2	msec
Quadrupole			
Mass Balance	70		% of 260 amu

1.2 Sodium Iodine – NaI

1480, RiaCalc WIZ, program 3,6 serial #4800419

Multi-Isotope Assay 15 ^{133}BaCO – Standards

Normalization of 8 ^{133}Ba October 14th, 2016 14:10:11

Total Counting Time:	60
Measured Counts:	158869
Decayed Activity:	1 0000
Standard Activity:	163955 cpm

End of Isotope Normalization

Normalization of 15 ^{60}Co October 14th, 2016 14:10:19

Total Counting Time:	60
Measured Counts:	32799
Decayed Activity:	1 0000
Standard Activity:	33308 cpm

End of Isotope Normalization

End of Counting

2 Preparations - Calculations

2.1 Preparations of Diluted Acids, EDTA and Ammonium Acetate – Ion Exchange

2.1.1 Preparation of HCl and HNO_3

The amounts of HCl and HNO_3 and water used to prepare the solutions in the developed method presented in chapter *3 Materials and Methods*, are calculated with equation 6 presented below;

$$C1 * V1 = C2 * V2 \tag{6}$$

C_1 represents start concentration, V_1 volume taken out from solution with concentration 1, V_2 desired volume of new solution, and C_2 desired concentration of new solution.

Example 1 – Calculations using Equation 6.

To make a 200 mL 6M HCl solution from concentrated HCl (12M), equation 6 was used:

C_1: 12	V_1: ?	C_2: 6M	V_2: 200 mL

$$V1 = \frac{6M * 200\ mL}{12M} = 100\ mL$$

This means that 100 mL of 12M HCl was dissolved in 100 mL DI-water to make a 200 mL solution of 6M HCl.

Example 2 – Preparation of 1% (V/V) Ultra-pure HNO_3

To prepare an 1% (V/V) ultra-pure HNO_3 solution, 1 mL ultra-pure HNO_3 were diluted in 99 mL DI-water, to make an 100 mL solution of 1% ultra-pure HNO_3.

2.1.2 Preparation of EDTA and Ammonium Acetate-solutions

Both the EDTA and Ammonium Acetate were found in solid state, so to prepare the solutions different approach had to be taken than the one presented in *2.1.1 Preparation of HCl and HNO_3*. The amounts of EDTA and Ammonium Acetate were calculated by using equation 7 and 8:

$$Concentration(M) = \frac{Mol}{Liter} \tag{7}$$

$$Mass\ (g) = Molar\ Mass\ \left(\frac{g}{mol}\right) * mol \tag{8}$$

These two equations were used to calculate the amounts of solid material needed to be dissolved in DI-water to make the appropriate concentrations. Example 3 shows how the calculations were done for both EDTA and Ammonium Acetate.

Example 3. Preparation of EDTA-solution

The desired concentration for the EDTA-solution was 0.01M, and the volume of the solution was 100 mL.

$$0{,}01M = \frac{x\,mol}{0{,}1\,L} \rightarrow x\,mol = 0{,}01M * 0{,}1\,L = 1 * 10^{-3}\,mol$$

$$Mass\ (g) = \frac{294.24\,g}{mol} * (1 * 10^{-3})\,mol = 0.2963\,g$$

0.2960 g of solid EDTA was dissolved in 100 mL DI-water to achieve the desired concentration of 0.01M EDTA in a 100 mL solution.

2.2 Preparation of ^{133}Ba Stock Solution

The ^{133}Ba solution had a known activity of 18.5 kBq in 1994. ^{133}Ba has a half-live of 10.4 years, which means that this solution of ^{133}Ba has undergone approximately two half-lives. The activity of this solution assumed to be approximately 4.63 kBq prior to measurement on NaI, per October 3rd 2016. It was assumed that an activity of around 50.0 Bq/mL (5.30 pg/L) ^{133}Ba would be sufficient as a yield or internal standard added to each water sample, so a stock solution was prepared with this in mind.

A stock solution of 9.30 ng/L (88.0 Bq/mL) was used as a yield monitor/ISTD for water samples, and was prepared by diluting 0.5 mL ^{133}Ba from a stock solution (471 ng/mL or 4.50 kBq/mL), 2.5 mL 12M HCl and DI-water to a total volume of 50.0 mL. The stock solution was prepared in a 50.0 mL Sartedt centrifuge tube.

A second stock solution of 18.4 ng/L (176 Bq/L) was used as a yield monitor/ISTD for soil samples, and was prepared by diluting 1 mL ^{133}Ba from a stock solution (471 ng/L or 4.50 kBq/mL), 2.5 mL 12M HCl and DI-water to a total volume of 50.0 mL. The stock solution was prepared in a 50.0 mL Sartedt centrifuge tube.

The original ^{133}Ba-solution was measured to make sure the activity of the solution was sufficient to make a protocol for measuring ^{133}Ba on NaI-detector, see attachment *1.3 Sodium Iodine – NaI*. The activity of the ^{133}Ba solution was measured to 16 3955 cpm 14/10-16 14:10:11. This means that the activity of the prepared stock solution is approximately 1640 cpm/mL or 5400 dpm/mL, which in turn means that a concentration of approximately 9.30 ng/L (88.0 Bq/mL) has been added to each water sample, since each water sample has been added 1 mL of this solution. The soil samples were added 1 mL with a concentration of 18.4 ng ^{133}Ba/L (176 Bq/L) .

It was made sure that the activity was appropriate according to the regulations concerning radiation protection and use of radiation from the Ministry of Health and Care Services in Norway (Lovdata a, 2010). An attachment found in Lovdata.no (Lovdata b, 2010) presents the working limits for all radionuclides cf. §2 fifth and sixth subsection. The working limit for ^{133}Ba is 10^6 Bq, which means that the certified C-lab at the Isotope laboratory can work with ^{133}Ba with an activity of 10 MBq. A stock-solution can be up to 100 MBq. The stock-solution for ^{133}Ba made for this experiment was way below the working limit for certified C-laboratories.

2.3 Preparation of ^{226}Ra Stock Solutions

2.3.1 Standard ^{226}Ra solution

The following information for the original standard ^{226}Ra solution was given:

B/2010

Concentration:	103.5 Bq/g
Mass:	10.07 g
ID:	A10124 – A10135/A10124
Product code:	R_{36}-02
Date of Calibration:	February 1st, 2010

Note: October 16th, 2012. Sealing broke, and solved in 50 mL (total solution) 1M HCl – 1.0 kBq/50 mL

2.3.2 Stock solution 20 Bq ^{226}Ra/L – Spiking test

A stock solution of approximately 547 pg ^{226}Ra/L (20.0 Bq ^{226}Ra/L) was prepared by diluting 1 mL of the original standard ^{226}Ra solution with 2% (V/V) HNO_3 and DI-water to a total volume of one liter. The stock solution was stored in 4˚C and in the dark.

This stock solution was used for spiking test, where ^{226}Ra was added to DI-water in different concentrations.

2.3.3 Stock solution 10 ng ^{226}Ra/L - Standards

A second stock solution of approximately 10.0 ng ^{226}Ra/L (366 Bq ^{226}Ra/L) was prepared by diluting 930 µL ^{226}Ra from the original standard solution with 1% v/v HNO_3 and DI-water to a total volume of 50.0 mL. The stock solution was stored in 4˚C and in the dark. This stock solution was used to prepare the external standards, for making the calibration curve.

2.4 Preparation of ^{226}Ra Standards – Calibration Curve

The ^{226}Ra standards were made by diluting the stock solution of 10.0 ng ^{226}Ra/L (366 Bq ^{226}Ra/L) was diluted to appropriate concentrations. All calculations presented in the table were calculated from equation 6:

$$C1 * V1 = C2 * V2 \tag{6}$$

C_1 represents start concentration, V_1 volume taken out from solution with concentration 1, V_2 desired volume of new solution, and C_2 desired concentration of new solution.

The concentrations of the standards, in pg ^{226}Ra/L and Bq/L, were as followed:

	Calibration blank	Standard 1	Standard 2	Standard 3	Standard 4
ng ^{226}Ra/L	0.00	0.0200	0.100	0.500	2.00
Bq ^{226}Ra/L	0.00	0.73	3.65	18.3	73.0

Table A1 shows the volume used to prepare the desired concentrations of the standards.

Table A1. Concentration and volume used to prepare the desired concentrations of the standards. The standards were used to make the calibration curve for quantification of ^{226}Ra in unknown samples.

	Desired Solution		Start Solution	
Standard	**Concentration [ng ^{226}Ra/L], C_2**	**Total Volume (mL), V_2**	**Concentration [ng ^{226}Ra/L], C_1**	**Volume (mL), V_1**
Calibration blank	0.000	50.0	10.0	0.00
Standard 1	0.0200	50.0	10.0	0.100
Standard 2	0.100	50.0	10.0	0.500
Standard 3	0.500	50.0	10.0	2.50
Standard 4	2.00	50.0	10.0	10.0

All standards, including calibration blank, contained 6.25 mL ^{133}Ba, the appropriate volume of ^{226}Ra from stock solution, 1% (V/V) ultra-pure HNO_3 and DI-water – to a total volume of 50.0 mL.

Example 4 – Calculations of v_1 in 0,02ng ^{226}Ra/L

c_1: 10.0 ng/L

v_1: ?

c_2: 0.0200 ng/L

v_2: 50.0 mL

$$V1 = \frac{\frac{0.0200ng}{L} * 50.0mL}{10.0ng/L} = 100\mu L$$

3 Recovery Testing

Table B1. Average values of ^{133}Ba, yield monitor, measured on NaI-detector for spiked samples, freshwater samples and the total. The blank, spiked samples, is not taken into account when calculating these values. The flow rate for the samples were 1,6 mL/min. Significant figures: 2.

Sample	Sample (DPM)	STD (DPM)	Recovery (%)	STD (%)	Sum of Recovery (%) for all steps	STD Sum (%)	Loss of yield (%)	STD Loss (%)	Recovery of IEX steps (%)	STD IEX (%)
Blank*	31		0.58		4.2		96		3.7	
0,0001	4000		71		97		3.1		25	
0,001	4500		82		99		1.2		17	
0,01	4600		85		100		0.26		17	
0,1	4300		78		100		-0.55		22	
O1	4800		88		100		-1.7		13	
O2	4500		83		97		3.5		14	
O3	4800		87		100		-0.20		13	
O4	3900		73		99		1.3		26	
O5	4300		77		87		13		10	
Spiked	4300		**79**	6.1	**99**	1.6	**1.0**	1.6	**20**	4.4
Orrefjell	3200		**82**	6.7	**97**	5.7	**3.1**	5.7	**15**	6.1
Total	4400		**81**	6.1	**98**	4.3	**2.2**	4.3	**17**	5.7

*Yield monitor, ^{133}Ba, was not added to this blank sample, thus explaining the “low recovery”.

Table B2. Average values of ^{133}Ba, yield monitor, measured on NaI-detector for produced water- and soil samples. The blank samples are not taken into account when calculating these values. The flow rate for the samples were 1,6 mL/min. Significant number; 2. Data can be found in attachment *3 Recovery Testing*, table *B3* and table *B4* .

Sample	Sample (DPM)	STD (DPM)	Recovery (%)	STD (%)	Sum of Recovery (%) for all steps	STD Sum (%)	Loss of yield (%)	STD Loss (%)	Recovery of IEX steps (%)	STD IEX (%)
PW Blank	4300		79		98		1.9		19	
PW Total	2800		51		72		27		21	
PW <0,45µm	3200		60		85		15		25	
PW <10kDa	3300		61		86		14		25	
Orrefjell 2.5	8600		66		88		12		22	
Orrefjell 3.3	8900		68		87		13		19	
Orrefjell 4.1	630		4,9		7.1		92		2.2	
Orrefjell Control 1	11000		86		91		8.8		4.9	
Orrefjell Control 2	12000		90		96		3.9		5.8	
Orrefjell Control 3	11000		88		95		5.1		7.1	

Alum shale	740		5.7		7.8		92		2.2	
CRM IAEA-135	11000		89		95		4.9		6.2	
Blank 1	10000		81		91		4.9		6.2	
Blank 2	11000		84		97		3.2		13	
Blank 3	10000		78		92		7.5		14	
Blank 4	11000		86		95		5.2		9.2	
Average Produced Water	3100	260	**57**	5.3	**81**	7.5	**19**	7.5	**24**	2.3
Average Soil	7900	4600	**62**	36	**71**	39	**29**	39	**8,6**	7.4
Average Soil*	10000	1300	**81**	11	**92**	4.0	**8,0**	4.0	**11**	7.4

*Average and standard deviation were calculated without soil sample 4.1 and alum shale.

Table B3. Data for recovery testing - presence of ^{133}Ba measured on NaI-detector – for ISTD-test.

Sample	Step	CPM (20 mL)	CCPM (20 mL)	DPM (20 mL)	DPM (50 mL)	Recovery (%)
ISTD-test	0.01M EDTA	7.4	6.7	22	55	1.0
	1.5M $C_2H_7NO_2$	140	140	460	1200	21
	0.03M HCl	62	62	200	500	9.1
	3M HCl	106	110	360		6.5
	Sample	1300	1300	4300		78
	Ba-133	1700	1700	5500		
	"Waste water"	11	9.1	30		
	Column material					

4 Digestion of Soil Samples

Table C1. Preparation of standards used for determination of Ba in CRM. The samples and standards were measured on ICP-MS. O_2 was used as a reaction gas for all elements. The acid solutions were either H_3PO_4, HNO_3 and HBF_4 or H_3PO_4 and HNO_3.

	Calibration Blank 1	Calibration Blank 2	Standard 1 6µg Ba/L	Standard 2 60µg Ba/L
	500 µL ISTD (200 µg Rh/L) 2.5 mL ultra-pure HNO_3 DI-water	500 µL ISTD (200 µg Rh/L) 2.5 mL ultra-pure HNO_3 0,5 mL acid-solution* DI-water	450 µL ISTD (200 µg Rh/L) 2.25 mL ultra-pure HNO_3 5 mL of Standard 2-solution 450 µL acid-solution* DI-water	100 µL 71A 100 µL 71B 200 µL 10mg Ba/L 0.5 mL acid-solution* 500 µL ISTD (200 µg Rh/L) 2.5 mL ultra-pure HNO_3 250 µL 1000 mg Al/L 250 µL 1000 mg Fe/L DI-water
Total Volume, mL	50	50	50	50

*A 50 mL acid-solution; 4 mL H_3PO_4, 2 mL HNO_3 and 2 mL HBF_4 diluted to 50 mL with DI-water.

Table C2. Concentration of Ba in mg/kg measured on ICP-MS after acid digestion on UW. The acid solutions were either H_3PO_4, HNO_3 and HBF_4 or H_3PO_4 and HNO_3. Significance figures: 2.

			135-> 135 Ba [O_2]	135 -> 151 Ba [O_2]	137 -> 137 Ba [O_2]	137 -> 153 Ba [O_2]
LOD (w/w)			0.3	0.7	0.1	1.0
LOQ (w/w)			0.95	2.5	0.36	4.5
Sample Name	**CRM**	**Certified Value**	**[mg/kg]**	**[mg/kg]**	**[mg/kg]**	**[mg/kg]**
A1	GBW 07401	590 ± 15	600	600	600	590
A2	GBW 07401	590 ± 15	640	640	650	640
A3	GBW 07403	1200 ± 30	1200	1200	1200	1100
A4	GBW 07403	1200 ± 30	1300	1300	1300	1300
A5	NIST 2710a	790 ± 36	760	770	760	760
A6	NIST 2710a	790 ± 36	770	750	770	770
A7	NIST 2711a	730 ± 15	740	740	740	730
A8	NIST 2711a	730 ± 15	700	670	690	690
A9	NCS DC 73325	180 ± 27	180	180	180	180
A10	NCS DC 73325	180 ± 27	180	180	180	180
A11	NCS DC 73007	410 ± 18	400	400	400	390
A12	NCS DC 73007	410 ± 18	390	390	390	380
A13	NIST 2709a	980 ± 28	970	970	980	960
A14	NIST 2709a	980 ± 28	950	960	950	950
A15			<1	<LOD	0,64	<LOD
A16			<1	<LOD	0,57	<LOD
A17			<1	<LOD	0,62	<LOD
1643H			530	530	530	540

Table C3. Recovery of Ba in percentage after acid digestion on UW. The acid solutions were either H_3PO_4, HNO_3 and HBF_4 or H_3PO_4 and HNO_3. Significance figures: 2.

Sample Name	CRM	Certified Value	135-> 135 Ba [O_2]	135->151 Ba [O_2]	137->137 Ba [O_2]	137->153 Ba [O_2]
		[mg/kg]	%	%	%	%
A1	GBW 07401	590 ± 15	100	100	100	99
A2	GBW 07401	590 ± 15	110	110	110	110
A3	GBW 07403	1200 ± 30	96	96	97	94
A4	GBW 07403	1200 ± 30	100	100	100	100
A5	NIST 2710a	790 ± 36	97	97	97	96
A6	NIST 2710a	790 ± 36	97	95	97	97
A7	NIST 2711a	730 ± 15	100	100	100	100
A8	NIST 2711a	730 ± 15	95	92	94	94
A9	NCS DC 73325	180 ± 27	100	100	100	100
A10	NCS DC 73325	180 ± 27	100	100	100	100
A11	NCS ZC 73007	410 ± 18	97	96	98	95
A12	NCS ZC 73007	410 ± 18	94	95	95	91
A13	NIST2709a	980 ± 28	100	99	100	98
A14	NIST2709a	980 ± 28	97	98	97	97

Table C4 Measured concentration in g/kg or mg/kg of barium, aluminum, iron and rare earth elements in certified reference materials. The samples are measured on ICP-MS. O_2 was used as a reaction gas for all elements. The digestion solutions used are HF, HNO_3 and HCl and a combination of HNO_3 and HCl. Significance figures: 2.

LOD (w/w)	0.040	0.30	3.0	0.04	0.09	3.0	0.030	0.30	0.02	0.30	0.70	0.10	1.0	0.020	0.040	0.0070	0.0080	0.0090
LOQ (w/w)	0.12	0.97	11	0.14	0.30	9.2	0.084	0.97	0.059	0.95	2.5	0.36	4.5	0.059	0.12	0.025	0.028	0.029
Element	Al	Al	Ti	Fe	Sr	Zr	Nb	Mo	Sn	Ba	Ba	Ba	Ba	La	Ce	Pr	Nd	Sm
CRM	g/kg	g/kg	mg/kg	g/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
GBW 07401	75	79	4800	36	160	140	15	1.5	5.6	590	600	600	590	32	70	7.1	27	5.2
GBW 07401	76	77	5100	38	170	130	16	1.7	5.9	640	640	650	640	34	75	7.4	28	5.5
GBW 07403	61	64	2200	13	380	82	7.7	<LOD	2.2	1200	1200	1200	1100	18	37	4.1	16	3.1
GBW 07403	66	68	2300	14	400	92	8.3	<1	2.2	1300	1300	1300	1300	19	39	4.4	17	3.1
NIST 2710a	55	55	2900	40	240	55	12	7.6	9.1	760	770	760	760	28	54	5.9	22	3.9
NIST 2710a	54	57	2900	41	240	56	11	7.6	9.4	770	750	770	770	28	53	5.7	22	3.7
NIST 2711a	66	63	3200	28	240	140	19	1.6	5.6	740	740	740	730	37	73	8.4	33	6.3
NIST 2711a	63	60	2900	27	210	110	17	1.6	5.9	690	670	690	690	34	68	7.7	30	5.7
NCS DC 73325	140	130	21000	120	26	290	63	2.9	3.7	180	180	180	180	41	98	10	43	9.7
NCS DC 73325	160	150	22000	130	27	160	61	3.2	3.6	180	180	180	180	43	100	11	45	9.9
NCS ZC 73007	95	93	5700	37	70	160	24	1.3	12	400	390	400	390	62	130	14	54	9.9
NCS ZC 73007	90	87	5400	36	66	75	22	0.99	16	390	390	390	380	60	130	14	51	9.7
NIST2709a	70	70	3200	33	240	68	8.3	1.7	1.7	970	970	980	960	22	43	4.8	19	3.6
NIST2709a	70	71	3100	33	230	43	8.1	1.6	1.5	950	960	950	950	21	42	4.6	18	3.5

Table C5. Measured concentration in g/kg or mg/kg of barium, aluminum, iron and rare earth elements in certified reference materials. The samples are measured on ICP-MS. O_2 was used as a reaction gas for all elements. The digestion solutions used are H_2PO_4, HNO_3 and H_2PO_4, HNO_3 and HBF_4. Significance figures: 2.

LOD (w/w)	0.0050	0.0050	0.0080	0.0040	0.010	0.010	0.0030	0.0020	0.0060	0.010	#NUM	0.0080	0.080	0.050	0.20	0.02	0.30	0.040
LOQ (w/w)	0.015	0.018	0.027	0.014	0.036	0.049	0.0093	0.0057	0.021	0.035	#NUM	0.027	0.26	0.17	0.66	0.065	0.86	0.14
Element	Eu	Eu	Eu	Eu	Gd	Dy	Ho	Er	Tm	Yb	Yb	Lu	Hf	Ta	W	Tl	Pb	Th
CRM	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
GBW 07401	1.00	0.98	1.0	0.94	4.5	4.4	0.90	2,5	0.38	2.5	2.7	0.36	3.9	1.0	3.5	0.93	100	11
GBW 07401	1.0	1.0	1.1	1.0	4.9	4.7	0.93	2.7	0.39	2.7	2.7	0.37	3.6	0.97	3.8	1.0	110	12
GBW 07403	0.83	0.69	0.89	0.67	2.7	2.6	0.53	1.5	0.28	1.5	1.7	0.26	2.4	0.59	1.1	0.50	30	5.5
GBW 07403	0.81	0.63	0.86	0.74	2.7	2.6	0.53	1.7	0.23	1.5	1.6	0.22	2.5	0.43	1.2	0.41	30	5.9
NIST 2710a	0.81	0.85	0.90	0.79	3.3	3.0	0.59	1.8	0.27	1.9	1.9	0.25	1.8	0.75	190	1.3	5300	16
NIST 2710a	0.80	0.77	0.88	0.71	3.1	2.8	0.56	1.7	0.26	1.8	1.6	0.26	1.8	0.63	190	1.4	5500	16
NIST 2711a	1.2	1.2	1.2	1.2	5.8	5.2	1.1	3.1	0.44	3.0	3.2	0.44	4.3	1.2	3.2	2.7	1500	14
NIST 2711a	1.1	1.0	1.1	1.1	5.1	5.1	0.97	2.9	0.42	2.9	3.1	0.42	3.4	0.97	3.1	2.7	1400	13
NCS DC 73325	3.3	3.3	3.3	3.2	9.0	6.4	1.0	2.7	0.34	2.2	2.0	0.28	6.9	3.6	1.5	0.19	15	8.8
NCS DC 73325	3.5	3.6	3.5	3.5	9.3	6.6	1.2	2.8	0.45	2.1	2.2	0.40	3.7	2.4	1.5	0.30	15	8.7
NCS ZC 73007	1.7	1.6	1.7	1.7	8.5	7.4	1.4	3.9	0.56	3.8	3.5	0.53	4.9	2.2	6.4	1.1	64	30
NCS ZC 73007	1.6	1.7	1.7	1.8	8.1	7.0	1.3	3.7	0.53	3.5	3.4	0.52	2.0	1.6	6.1	1.1	63	28
NIST2709a	0.87	0.94	1.00	0.86	3.3	3.0	0.59	1.9	0.26	1.8	1.7	0.26	2.0	0.59	1.8	0.53	19	10
NIST2709a	0.86	0.83	0.95	0.97	2.9	2.8	0.58	1.7	0.23	1.5	1.6	0.23	1.3	0.41	2.0	0.52	18	9.5

5 Determination of ^{226}Ra in Unknown Environmental Samples

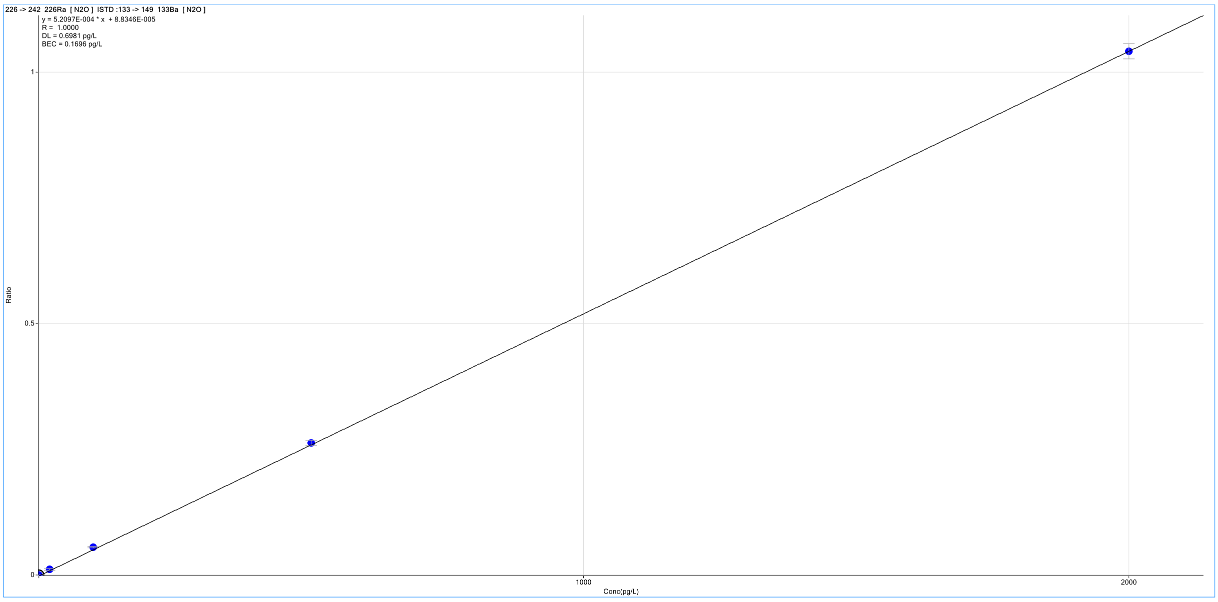

Figure D1. Standard Curve used for quantification of ^{266}Ra in unknown environmental samples. The y-axis represents (cps ^{226}Ra/cps ^{133}Ba) whereas the x-axis represents the concentration of ^{226}Ra in pg/L.

Table D1. Concentration in pg/L ^{226}Ra in upconcentrated blank samples, measured with S-lens. The concentrations are corrected with ^{133}Ba as internal standard. Limit of Detection and Limit of Quantification is presented for both ^{226}Ra and ^{228}Ra in 2 L samples and 5 gram soil sample. ^{226}Ra-results given with two significant figures, and results for ^{228}Ra are given with one significant figure.

	^{226}Ra -> ^{242}Ra [N$_2$O] 8 mL sample		^{228}Ra -> ^{244}Ra [N$_2$O] 8 mL sample	
Sample Name	**Conc. [pg/L]**	**Conc. RSD %**	**Conc. Calculated from ^{226}Ra [pg/L]**	**CPS**
PW Blank	6.0	56	0.3	0.09
Soil Blank 1	16	10	0.5	0.1
Soil Blank 2	5.9	37	0.4	0.09
Soil Blank 3	5.6	40	0.4	0.09
Soil Blank 4	9.1	41	0.4	0.09

	^{226}Ra → ^{242}Ra [pg/L] 2 L sample	^{226}Ra → ^{242}Ra [pg/kg] 5 gram sample	^{228}Ra → ^{244}Ra [pg/L] 2 L sample	^{228}Ra → ^{244}Ra [pg/kg] 5 gram sample
LOD:	0.052	21	0.0008	0.3
LOQ:	0.17	69	0.003	1.

5.1 Measurement of Polyatomic Interferences

Table D2. Data for measurement of polyatomic interferences for both ^{133}Ba and ^{226}Ra in two gas modes on ICP-QQQ. Significance figures: 2.

Sample Name	^{133}Ba -> ^{149}Ba [N_2O]			^{226}Ra -> ^{242}Ra [N_2O]		
	[pg/L]	CPS	Conc. RSD %	[pg/L]	CPS	Conc. RSD %
Pb 20 µg/L	6.0	1.0	100	0.00	0	N/A
Cs 20 µg/L	2.3	0.60	160	0.13	0.04	220
W 20 µg/L	1.3	0.48	110	0	0	N/A
71 ABD 20 µg/L*	2.3	0.60	71	0.13	0.04	220
Sample Name	**^{133}Ba -> ^{149}Ba [No gas]**			**^{226}Ra -> ^{242}Ra [No gas]**		
	[pg/L]	**CPS**	**Conc. RSD %**	**[pg/L]**	**CPS**	**Conc. RSD %**
Pb 20 µg/L**	500	690	4.1	0.19	0.28	270
Cs 20 µg/L	10000000	10000000	1.6	-0.048	0.080	N/A
W 20 µg/L	1400	1600	15	4.7	4.1	30
71 ABD 20 µg/L*	9600000	9600000	1.9	5.0	4.3	14

5.2 Water Samples

Table D3. Sample details for freshwater samples used for optimization of instrument parameters on ICP-MS. Samples are freshwater from Orrefjell, Troms Norway.

Sample no.	Location	Volume (mL)	Date of Sampling
1	E16/16 Ytrebekken	1900	7/9-2016
2	E16/16 Ytrebekken	1800	7/9-2016
3	Private well	1950	8/9-2016
4	Station 7 Kvernbekken	2000	7/9-2016

Table D4. Sample sequence with sample number and recovery percentage of ^{133}Ba. The recovery of ^{133}Ba is measured on ICP-MS with gas mode "nitrous oxide". Significant figures: 2.

Sample	Recovery of yield monitor %, NaI		Recovery of yield monitor %, ICP-MS	
	Recovery (%)	Relative Uncertainty (%)	Recovery (%)	Relative Standard Deviation (%)
Blank – spiked sample*	0	22		
0.0001Bq/L	71	0.93	70	2.6
0.001Bq/L	82	0.87	69	5.2
0.01Bq/L	86	0.86	73	3.1
0.1Bq/L	78	0.89	65	6.5
Orrefjell 1	88	0.84	61	3.5
Orrefjell 2	83	0.87	59	2.2
Orrefjell 3	87	0.85	52	2.2
Orrefjell 4	73	0.93	53	6.8

*Blank sample was not added ^{133}Ba as of personal error.

5.3 Soil Samples

Project Name: Case Orrefjell

Activity: 548 ± 15 Bq/kg (NRPA Tromsø)

Table D5. GPS-coordinates for Soil Samples from Orrefjell (O1-O3).

Station	Name	Lat D	Lat M	LatDecMin	LatDir	Long D	Long M	LongDecMin	LongDir
ST2	Orre high	68	53	5849	N	18	05	8442	E

Table D6. Data for Determination of ^{226}Ra in Soil Samples for master project by Shcöpke, C. 2017, measured by Ge-detector, performed by NRPA, Tromsø. Significance figures has not been taken into account.

Sample	Soil dry weight, grams	shale dry weight, grams	^{226}Ra Activity or MDA, Bq/kg dry weight	err, Bq/kg, 2σ
Soil 1 (5 replicates)				
1.1			91.2	4.8
1.2			92.7	2
1.3			96.3	2
1.4			93.3	2
1.5			94.4	4.1
Soil 2 (5 replicates)				
2.1	550.5		690	15
2.2	550		695	15
2.3	550.5		702	15
2.4	549.9		693	15
2.5	550.1		675	14
Soil 2 + 5% Alum shale (5 replicates)				
3.1	522.6	27.5	742	16
3.2	522.4	27.5	771	16
3.3	522.7	27.4	787	17
3.4	522.7	27.4	777	17
3.5	522.4	27.4	765	16
Soil 2 + 25% Alum shale (5 replicates)				
4.1	412.4	137.5	1015	21
4.2	412.4	137.5	1002	21
4.3	412.4	137.6	1023	22
4.4	412.4	137.6	1030	22
4.5	412.4	137.8	1052	22

6 “Which elements are present in the samples?”

Table E1. Preparation of External Standards used to determine which other elements were present in the samples.

	Calibration Blank	Standard 1	Standard 2
Ultra-pure HNO_3, mL	1	1	1
Total volume, mL	50	50	50
Solutions	DI-water	5 mL of Standard 2 DI-water	250 μL 71A 10 mg/L – 50 μg/L 250 μL 71B 10 mg/L – 50 μg/L 250 μL 71D 10 mg/L – 50 μg/L 250 μL Li 10 mg/L – 50 μg/L 100 μL Na 10 g/L – 20 mg/L 100 μL Fe 10 g/L – 20 mg/L 1 mL Mg 1 g/L – 20m g/L 100 μL Al 10 g/L – 20 mg/L 100 μL K 10 g/L – 20 mg/L 250 μL Ca 10 g/L – 50 mg/L 100 μL Mn 1 g/L – 2 mg/L 100 μL Cu 1 g/L – 2 mg/L 100 μL Zn 1 g/L – 2 mg/L 500 μL Sr 1 g/L – 10 mg/L 500 μL Ba 1 g/L – 10 mg/L 100 μL Hg 2 μg/L – 4 μg/L 100 μL Pb 100 μg/L – 200 μg/L DI-water

6.1 Water Samples

Table E2. Concentrations of elements in Produced Water and Formation Water. Significance figures: 2.

	Sample:	K1	K2	PW 10 kDa	PW 0.45 μm	PW total	1643H-control	
	Yield, %:	13.5	14.3	61	60	51		
Element	**Unit**	**Conc.**	**Conc.**	**Conc.**	**Conc.**	**Conc.**	**Conc.**	**Unit**
Li	μg/L	<LOD	<LOD	17	1,4	2.1	16	μg/L
Be	μg/L	0.044	0.05	0.078	0.097	1.1	14	μg/L
Na	mg/L	30	9.1	56	14	14	20	mg/L
Mg	mg/L	6.2	1.9	2.6	1.4	5.9	8.0	mg/L
Al	mg/L	0.96	0.31	1.3	1.9	6.7	0.14	mg/L
K	mg/L	3.1	0.93	3	1.6	7	1.9	mg/L
Ca	mg/L	66	38	40	25	150	33	mg/L
Ti	mg/L	0.0069	0.042	0.1	0.099	0.33	0.00	mg/L
V	μg/L	3.7	3.8	8	9.6	21	39	μg/L
Cr	μg/L	42	39	180	170	110	20	μg/L
Mn	mg/L	0.013	0.015	0.048	0.045	0.17	0.040	mg/L
Fe	mg/L	0.31	1.4	2.4	3.5	16	0.090	mg/L
Co	μg/L	1.1	1.2	6.3	28	10	27	μg/L

Ni	**µg/L**	30	28	61	61	49	63	µg/L
Cu	**mg/L**	0.035	0.033	0.061	0.045	0.062	0.020	mg/L
Zn	**mg/L**	0.047	0.048	1.1	1	1.7	0.080	mg/L
Ge	**µg/L**	0.014	0.0057	0.38	0.37	0.37	0.010	µg/L
As	**µg/L**	1.1	0.98	1.4	1.4	2.6	62	µg/L
Se	**µg/L**	0.84	0.51	0.48	0.076	0.32	12	µg/L
Rb	**µg/L**	3.4	1.2	8.7	4.5	28	14	µg/L
Sr	**g/L**	0.13	0.13	1.2	1.2	1.5	0.33	mg/L
Y	**µg/L**	1.8	0.73	7.2	9.1	21	0.00	µg/L
Zr	**µg/L**	4.9	2.9	13	8.7	7.3	5.2	µg/L
Nb	**µg/L**	0.093	0.089	0.78	1.5	8.1	1.0	µg/L
Mo	**µg/L**	5.3	4.9	12	12	8.8	130	µg/L
Ag	**µg/L**	6.3	4.7	6.3	5.1	10	1.1	µg/L
Cd	**µg/L**	0.051	0.024	0.28	0.14	0.66	7.0	µg/L
In	**µg/L**	0.18	0.12	0.45	0.42	0.7	0.00	µg/L
Sn	**µg/L**	49	27	120	120	200	0.010	µg/L
Sb	**µg/L**	1.3	0.91	1.7	1.6	1.3	61	µg/L
Te	**µg/L**	0.033	0.03	0.12	0.055	0.09	1.1	µg/L
Cs	**µg/L**	0.31	0.13	0.77	0.51	4.2	14	µg/L
Ba	**g/L**	0.0021	0.0022	7.6	7.4	7.8	0.51	mg/L
La	**µg/L**	1.1	0.57	49	52	62	1.2	µg/L
Ce	**µg/L**	2.3	1.2	1.7	3.5	16	1.2	µg/L
Pr	**µg/L**	0.29	0.15	0.29	0.55	2.6	1.2	µg/L
Nd	**µg/L**	1	0.59	3.1	5	19	1.1	µg/L
Sm	**µg/L**	0.17	0.1	0.3	0.91	5	1.0	µg/L
Eu	**µg/L**	0.1	0.031	160	170	180	1.1	µg/L
Gd	**µg/L**	0.19	0.12	0.28	0.75	4.4	1.1	µg/L
Tb	**µg/L**	0.029	0.024	0.055	0.12	0.61	0.00	µg/L
Dy	**µg/L**	0.16	0.13	0.22	0.59	3.1	1.1	µg/L
Ho	**µg/L**	0.034	0.027	0.061	0.1	0.57	1.1	µg/L
Er	**µg/L**	0.086	0.075	0.13	0.29	1.5	1.0	µg/L
Tm	**µg/L**	0.016	0.014	0.029	0.031	0.17	1.1	µg/L
Yb	**µg/L**	0.068	0.14	0.16	0.29	0.99	1.1	µg/L
Lu	**µg/L**	0.015	0.016	0.028	0.034	0.12	1.1	µg/L
Hf	**µg/L**	0.1	0.072	0.46	0.26	0.28	0.040	µg/L
Ta	**µg/L**	0.02	0.016	0.36	0.093	0.03	0.030	µg/L
W	**µg/L**	0.15	0.082	1	0.72	0.83	0.020	µg/L
Hg	**µg/L**	0.12	0.076	0.23	0.12	0.5	0.39	µg/L
Pb	**µg/L**	4.9	4.5	38	12	39	20	µg/L
Bi	**µg/L**	0.78	0.74	3.6	3.4	1.5	0.010	µg/L
Th	**µg/L**	0.057	0.038	0.46	2.1	13	0.99	µg/L
U	**µg/L**	14	12	0.51	1.9	4.1	0.96	µg/L

6.2 Soil Samples

Table E3. Concentrations of elements in soil samples from Orrefjell, alum shale and Certified Reference Material IAEA-135. Significance figures: 2.

	Sample:	O1	O2	O3	2.5	3.3	4.1	Alum Shale	IAEA 135	1643H	
	Yield, %:	86	90	88	66	68	5	6	89		
Element	Unit	Conc.	Conc.	Conc.	Conc.	Conc.	Conc.	Conc.	Conc.	Conc.	Unit
Li	µg/L	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	16	µg/L
Be	µg/L	19	9.9	5.0	0.046	0.079	5.2	5.3	61	14	µg/L
Na	mg/L	2.5	1.8	1.7	2.6	2.0	2.8	2.3	2.2	20	mg/L
Mg	mg/L	1.1	0.26	0.19	3.4	4.6	240	210	58	8.0	mg/L
Al	g/L	0.73	0.56	0.44	0.84	0.83	5.1	5.2	3.5	0.14	mg/L
K	mg/L	1.3	0.33	0.22	0.51	0.56	2.2	1.8	0.45	1.9	mg/L
Ca	mg/L	0.17	0.077	0.085	0.34	0.41	0.97	0.95	0.25	33	mg/L
Ti	mg/L	3.7	2.8	1.6	33	27	110	18	69	0.00	mg/L
V	mg/L	0.9	0.53	0.25	0.0076	0.025	2.4	1.2	3.0	39	µg/L
Cr	mg/L	0.23	0.18	0.14	1.2	1.2	2.5	1.7	3.8	20	µg/L
Mn	mg/L	1.5	0.48	0.91	0.4	0.47	13	12	4.6	0.040	mg/L
Fe	g/L	0.32	0.18	0.1	0.17	0.18	0.94	0.34	1.5	0.09	mg/L
Co	µg/L	46	28	31	4.3	6.3	380	590	72	27	µg/L
Ni	mg/L	0.25	0.16	0.14	0.04	0.064	5.5	11	0.38	63	µg/L
Cu	mg/L	0.98	0.55	0.21	0.034	0.027	0.052	0.051	0.33	0.020	mg/L
Zn	mg/L	0.66	0.15	0.089	0.051	0.054	1.4	1.4	0.17	0.080	mg/L
Ge	µg/L	0.062	0.074	0.04	0.073	0.06	0.22	0.12	0.16	0.010	µg/L
As	µg/L	9.2	5.2	3.0	2.0	1.9	3.1	1.6	3.7	62	µg/L
Se	µg/L	0.0016	0.19	0.00026	0.066	0.2	0.38	0.0053	<LOD	12	µg/L
Rb	µg/L	4.8	1.3	0.62	15	17	36	33	4.7	14	µg/L
Sr	mg/L	13	11	11	27	33	31	22	13	0.33	mg/L
Y	mg/L	0.24	0.24	0.18	4.8	6.8	8.5	10	1.6	0.00	µg/L
Zr	µg/L	18	6.9	2.3	65	27	130	34	28	5.2	µg/L
Nb	µg/L	0.17	0.12	0.099	2.0	1.4	17	4.2	5.8	1.0	µg/L
Mo	µg/L	5.4	5.1	4.9	4.8	5	11	12	5.7	130	µg/L
Ag	µg/L	5.4	5.2	5.7	7.2	4.5	5.8	3.6	6.2	1.1	µg/L
Cd	µg/L	8.7	2.4	0.91	0.16	0.82	41	46	3.1	7.0	µg/L
In	µg/L	0.94	0.66	0.34	0.16	0.12	0.82	0.37	2.0	0.00	µg/L
Sn	µg/L	60	58	55	33	20	86	21	110	0.010	µg/L
Sb	µg/L	10	7.8	7.4	42	37	220	67	210	61	µg/L
Te	µg/L	0.38	0.069	0.048	0.053	0.022	0.19	0.073	0.3	1.1	µg/L
Cs	µg/L	0.37	0.079	0.032	1.6	1.4	3.9	2.3	0.17	14	µg/L
Ba	mg/L	29	27	25	210	220	21	8.5	38	0.51	mg/L
La	mg/L	0.26	0.26	0.21	6.8	4.8	9.1	8.1	1.7	1.2	µg/L
Ce	mg/L	0.58	0.6	0.48	12	10	18	17	4.0	1.2	µg/L
Pr	mg/L	0.1	0.11	0.08	1.7	1.6	2.4	2.2	0.51	1.2	µg/L

Nd	**mg/L**	0.33	0.36	0.27	6.0	6.0	8.8	8.3	1.9	1.1	µg/L
Sm	**mg/L**	0.062	0.067	0.051	1.1	1.2	1.7	1.6	0.39	1.0	µg/L
Eu	**µg/L**	12	13	9.5	270	290	390	340	76	1.1	µg/L
Gd	**mg/L**	0.054	0.057	0.043	1.0	1.2	1.5	1.5	0.35	1.1	µg/L
Tb	**µg/L**	8.6	9.0	6.5	160	190	240	240	56	0.00	µg/L
Dy	**mg/L**	0.047	0.049	0.035	0.85	1.0	1.4	1.4	0.32	1.1	µg/L
Ho	**µg/L**	9.5	9.8	6.8	180	240	320	320	64	1.1	µg/L
Er	**µg/L**	24	25	17	460	590	750	750	170	1.0	µg/L
Tm	**µg/L**	3.3	3.6	2.2	62	91	120	120	25	1.1	µg/L
Yb	**µg/L**	20	22	12	340	520	670	660	150	1.1	µg/L
Lu	**µg/L**	2.9	3.3	1.8	50	77	99	100	23	1.1	µg/L
Hf	**µg/L**	0.50	0.21	0.086	1.5	0.81	4.0	0.97	1.3	0.040	µg/L
Ta	**µg/L**	0.032	0.061	0.012	0.041	0.051	1.8	0.42	1.3	0.030	µg/L
W	**µg/L**	0.18	0.14	0.13	0.21	0.26	3.3	1.2	0.64	0.020	µg/L
Hg	**µg/L**	3.2	2.0	0.55	0.45	0.28	1.3	0.44	2.8	0.39	µg/L
Pb	**µg/L**	670	180	24	8.0	9.7	220	60	360	20	µg/L
Bi	**µg/L**	4.6	1.6	0.97	8.5	7.7	46	12	5.2	0.010	µg/L
Th	**µg/L**	1.5	2.1	1.3	120	88	120	66	37	0.99	µg/L
U	**mg/L**	0.58	0.5	0.48	1.8	1.4	2.3	1.7	0.11	0.96	µg/L

Table E4. Sample Details for PCA-test performed in Minitab16. Yield recovery is given with two significance figures,

	Sample Name	Yield, %	Sample Type
A	Orrefjell 1	86	Soil
A	Orrefjell 2	90	Soil
A	Orrefjell 3	88	Soil
A	Sample 2.5	66	Soil
A	Sample 3.3	68	Soil
A	Sample 4.1	5	Soil
A	Alum Shale	6	Soil
A	IAEA-135	89	Soil
B	Formation Water, K1	13	Water
B	Formation Water, K2	14	Water
B	PW 10 kDa	61	Water
B	PW 0.45µm	60	Water
B	PW Total	51	Water

7 Statistics

7.1 One-Way ANOVA: Comparison of ICP-QQQ and Ge-Detector Schöpke, C. 2017

One-Way ANOVA: Ge, Bq/kg; ISTD, Bq/kg; Yield, Bq/kg

```
Source DF   SS   MS   F   P
Factor  2  5318  2659 0,08 0,927
Error   6 208372 34729
Total   8 213690

S = 186,4  R-Sq = 2,49%  R-Sq(adj) = 0,00%

                Individual 95% CIs For Mean Based on
                Pooled StDev
Level      N  Mean StDev ------+---------+---------+---------+---
Ge, Bq/kg   3 825,7 173,3    (-----------------*-----------------)
ISTD, Bq/kg  3 775,7 266,6 (-----------------*----------------)
Yield, Bq/kg 3 828,7  55,5    (----------------*-----------------)
                ------+---------+---------+---------+---
                  600     750     900    1050
Pooled StDev = 186,4

Grouping Information Using Tukey Method
       N  Mean Grouping
Yield, Bq/kg 3 828,7 A
Ge, Bq/kg   3 825,7 A
ISTD, Bq/kg  3 775,7 A

Means that do not share a letter are significantly different.

Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 97,80%
Ge, Bq/kg subtracted from:
        Lower Center Upper -------+---------+---------+---------+--
ISTD, Bq/kg  -517,0  -50,0 417,0 (--------------*---------------)
Yield, Bq/kg -464,0   3,0 470,0  (--------------*---------------)
                   -------+---------+---------+---------+--
                     -300      0     300     600
ISTD, Bq/kg subtracted from:
        Lower Center Upper -------+---------+---------+---------+--
Yield, Bq/kg -414,0  53,0 520,0   (---------------*--------------)
                   -------+---------+---------+---------+--
                     -300      0     300     600
```

7.2 One-Way ANOVA: Comparison of Yield- and ISTD corrections in Spiked Samples (November/March)

One-Way ANOVA: pg/L Yield N; pg/L Yield M; pg/L ISTD No; pg/L ISTD Ma; ...

```
Source DF   SS  MS   F   P
Factor  4  0,37 0,09 0,04 0,996
Error  10 21,62 2,16
Total  14 21,98

S = 1,470  R-Sq = 1,66%  R-Sq(adj) = 0,00%

Level         N  Mean StDev
pg/L Yield November 3 0,720 1,027
pg/L Yield March   3 0,963 1,422
pg/L ISTD November  3 1,082 1,581
pg/L ISTD March   3 1,189 1,747
Initial Conc, pg/L  3 0,999 1,478

           Individual 95% CIs For Mean Based on Pooled StDev
Level         +---------+---------+---------+---------
pg/L Yield November   (---------------*---------------)
pg/L Yield March     (---------------*---------------)
```

```
pg/L ISTD November     (---------------*---------------)
pg/L ISTD March       (---------------*---------------)
Initial Conc, pg/L     (--------------*---------------)
            +---------+---------+---------+---------
           -1,2    0,0    1,2    2,4

Pooled StDev = 1,470

Grouping Information Using Tukey Method
           N  Mean Grouping
pg/L ISTD March   3 1,189 A
pg/L ISTD November  3 1,082 A
Initial Conc, pg/L  3 0,999 A
pg/L Yield March   3 0,963 A
pg/L Yield November 3 0,720 A

Means that do not share a letter are significantly different.

Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99,18%

pg/L Yield November subtracted from:
           Lower Center Upper
pg/L Yield March  -3,704  0,243 4,190
pg/L ISTD November -3,586  0,362 4,309
pg/L ISTD March   -3,478  0,469 4,417
Initial Conc, pg/L -3,668  0,279 4,226

          -------+---------+---------+---------+--
pg/L Yield March   (---------------*---------------)
pg/L ISTD November   (--------------*---------------)
pg/L ISTD March    (---------------*---------------)
Initial Conc, pg/L  (---------------*---------------)
          -------+---------+---------+---------+--
            -2,5    0,0    2,5    5,0

pg/L Yield March subtracted from:
           Lower Center Upper
pg/L ISTD November -3,829  0,119 4,066
pg/L ISTD March   -3,721  0,226 4,174
Initial Conc, pg/L -3,911  0,036 3,983

          -------+---------+---------+---------+--
pg/L ISTD November  (--------------*---------------)
pg/L ISTD March    (---------------*---------------)
Initial Conc, pg/L  (---------------*---------------)
          -------+---------+---------+---------+--
            -2,5    0,0    2,5    5,0

pg/L ISTD November subtracted from:
           Lower Center Upper
pg/L ISTD March   -3,840  0,108 4,055
Initial Conc, pg/L -4,030 -0,083 3,865

          -------+---------+---------+---------+--
pg/L ISTD March    (--------------*---------------)
Initial Conc, pg/L  (---------------*--------------)
          -------+---------+---------+---------+--
            -2,5    0,0    2,5    5,0

pg/L ISTD March subtracted from:
           Lower Center Upper
Initial Conc, pg/L -4,138 -0,190 3,757

          -------+---------+---------+---------+--
Initial Conc, pg/L (---------------*---------------)
```

```
         -------+---------+---------+---------+--
           -2,5      0,0      2,5      5,0
```

7.3 One-Way ANOVA: Comparison of Yield- and ISTD corrections in Spiked Samples (March)

One-Way ANOVA: Initial Conc, pg/L; pg/L Yield March; pg/L ISTD March

```
Source  DF    SS   MS    F    P
Factor   2  0,09 0,04 0,02 0,982
Error    6 14,51 2,42
Total    8 14,60

S = 1,555  R-Sq = 0,61%  R-Sq(adj) = 0,00%

Level         N  Mean StDev
Initial Conc, pg/L 3 0,999 1,478
pg/L Yield March  3 0,963 1,422
pg/L ISTD March   3 1,189 1,747

          Individual 95% CIs For Mean Based on Pooled StDev
Level         +---------+---------+---------+---------
Initial Conc, pg/L   (-----------------*------------------)
pg/L Yield March    (-----------------*-----------------)
pg/L ISTD March     (-----------------*-----------------)
            +---------+---------+---------+---------
          -1,2     0,0      1,2      2,4

Pooled StDev = 1,555

Grouping Information Using Tukey Method
          N  Mean Grouping
pg/L ISTD March   3 1,189 A
Initial Conc, pg/L 3 0,999 A
pg/L Yield March  3 0,963 A

Means that do not share a letter are significantly different.


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 97,80%

Initial Conc, pg/L subtracted from:
          Lower Center Upper
pg/L Yield March -3,933 -0,036 3,861
pg/L ISTD March  -3,707  0,190 4,087

         ------+---------+---------+---------+---
pg/L Yield March (---------------*--------------)
pg/L ISTD March  (---------------*--------------)
         ------+---------+---------+---------+---
           -2,5      0,0      2,5      5,0

pg/L Yield March subtracted from:
         Lower Center Upper
pg/L ISTD March -3,671  0,226 4,123

         ------+---------+---------+---------+---
pg/L ISTD March  (---------------*--------------)
         ------+---------+---------+---------+---
```

7.4 One-Way ANOVA: Comparison of ICP-QQQ (yield/ISTD) and Ge-Detector for Orrefjell Parallel Samples (O1-O3)

One-way ANOVA: Reference, Bq/kg; ISTD, Bq/kg; Yield, Bq/kg; No Corr., Bq/kg

```
Source DF   SS  MS   F    P
Factor  3  4614 1538 1,15 0,387
Error   8 10725 1341
Total  11 15339

S = 36,61  R-Sq = 30,08%  R-Sq(adj) = 3,86%

                  Individual 95% CIs For Mean Based on
                  Pooled StDev
Level        N  Mean StDev  -+---------+---------+---------+--------
Reference, Bq/kg 3 548,00  0,00     (-----------*-----------)
ISTD, Bq/kg    3 535,00  0,00   (-----------*-----------)
Yield, Bq/kg   3 523,33 42,25  (-----------*-----------)
No Corr., Bq/kg  3 576,00 59,81        (-----------*-----------)
                   -+---------+---------+---------+--------
                  480     520     560     600

Pooled StDev = 36,61

Grouping Information Using Tukey Method
         N  Mean Grouping
No Corr., Bq/kg  3 576,00 A
Reference, Bq/kg 3 548,00 A
ISTD, Bq/kg    3 535,00 A
Yield, Bq/kg   3 523,33 A

Means that do not share a letter are significantly different.
```

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