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Separation and measurement of alpha-emitting actinides from different matrices at Loviisa NPP

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| <p>Measurement of alpha-active actinides requires separation from other alpha emitting radionuclides. A method of actinide separation was needed for the primary coolant water of Loviisa Nuclear Power Plant. A method published by Eichrom Ltd was chosen to be evaluated, this method utilises a vacuum box with stacked TEVA / TRU columns which speeds up and eases the analysis process.</p> <p>The method can be used to separate americium, curium, plutonium and uranium from a water samples and it gave excellent results both with reference samples and primary coolant water. The separation was also tested with other more difficult matrices: ion exchange resins, surface swipes, aerosol filters and process waste waters. Pretreatment methods for these matrices were assessed and tested to reduce the sample to a soluble form that could be loaded to the separation system. DGA resin based methods were tested for both gross-alpha and nuclide specific analyses. The gross-alpha method with DGA was fast, efficient and reliant.</p> <p>Gross alpha counting samples could be produced within hours and element fraction samples could be produced in 1 - 2 days. This combined with the good recoveries of all fractions meant shorter counting times to reach the minimal detectable activities (MDAs) required.</p> <p>The literature review part takes a look into recent interesting topics related to actinide separation and analysis from similar matrices discussed in the the experimental section. Different extraction chromatography resins are discussed.</p> | | | |
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Preface

I got a chance to perform this work at Loviisa NPP in 2020. Most of this work was done during the exceptional times experienced during the COVID-19 pandemic that shut down large parts of the society and changed our behavior. The pandemic had many unforeseen consequences that had their effect on this work but luckily there were no obstacles to large.

I would like to thank my supervisor Susanna Salminen-Paatero from University of Helsinki and both Satu Rautio and Satu Kangas from Fortum for their amazing support and guidance during the course of this work. I would like to thank Jarno, Leena, Joonas, Riku and the whole chemistry group at Loviisa for their support with the lab. I also thank my family and friends for their support and advice.

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List of Acronyms

An General term for an element in the actinide group

BWR Boiling water reactor

CRUD Corrosion and wear products, originally Chalk River Unidentified Deposit, a precipitate found on fuel cladding surfaces

DGA DiGlycolAmide, an extraction chromatographic resin

GWd/t Gigawatt-days/ton (heavy metal: U, Th, Pu) describes how much the fuel has been utilized, burnup

HLLW high-level liquid waste

INES International Nuclear and Radiological Event Scale.

k' Free column volumes to peak maxima

LO1 / LO2 Loviisa (Fortum) units 1 and 2

LOCA Loss Of Coolant Accident

MA Minor actinide

MDA Minimum Detectable Activity

MOX mixed oxide fuel, fuel containing both U and Pu as fissile material

MWe Megawatts, electric

MWt Megawatts, thermal

NORM Naturally Occuring Radioactive Material

NPP Nuclear power plant

OL1 / OL2 / OL3 Olkiluoto (TVO) units 1 - 3

OLC Operational Limits and Conditions, also TTKE

PCP Primary coolant pump

pH_T pH at a given temperature, in this work 300 °C.

PWR pressurised water reactor

RPV Reactor pressure vessel

STUK Säteilyturvakeskus, Finnish Radiation and Nuclear Safety Authority

TEVA tetravalent actinides, an extraction chromatographic resin

TRU an extraction chromatographic resin or transuranium elements

TTKE Turvallisuustekniset käyttöehdot, also OLC

TWh Terawatt hours

UTEVA Uranium and tetravalent actinides, an extraction chromatographic resin

VBS Vacuum box system

VVER From Russian: водо-водяной энергетический реактор; vodo-vodyanoi energetichesky reaktor; water-water energetic reactor

YVL Ydinturvallisuusohjeet, regulatory guides on nuclear safety and security

1 Introduction

Loviisa nuclear power plant is owned and operated by Fortum Oyj, formerly known as Imatran Voima (IVO). The site has two VVER-440 (from Russian: водо-водяной энергетический реактор; vodo-vodyanoi energetichesky reaktor; water-water energetic reactor) pressurised water reactors (PWR) (Units LO1 & LO2) which have been updated from their initial design capability of 440 MWe to 507 MWe / 1500 MWt generating capability each. They generate about 8 TWh of electricity annually, which is about 10 % of the electricity production in Finland. The construction of the plant took 10 years and the units were commissioned in 1977 and 1980. Their operating licences are valid until 2027 and 2030 respectively. They were designed with the most advanced safety requirements at the time, and they incorporate a wide range of western technology. The units are based on the VVER-440V213 design but the amount of modifications made to the plant, makes the units unique among VVER-440 type reactors.

The radiochemistry section is part of the Operation Unit and the Operation Chemistry Group at the Loviisa Nuclear Power Plant. The main responsibilities of radiochemistry at Loviisa are process monitoring and monitoring of the radioactive releases. Main tools for radiochemistry are gamma spectrometers, a liquid scintillation detector, a proportional counter and an alpha spectrometer. There are also some portable alpha/beta counters intended to replace / augment the proportional counter and add to the fieldable detectors that the radiation protection organisation has. Some radiochemical separations are routinely performed by the radiochemistry section, these are mainly some long lived beta emitters (Fe-55, Ni-63).

The Finnish regulatory guides on nuclear safety and security (Ydinturvallisuusohjeet, YVL) are published by the Finnish Radiation and Nuclear Safety Authority (Säteilyturvakeskus, STUK). The mandate for these regulations come from the Nuclear Energy Act (990/1987), Section 7r, which states that STUK *"shall specify detailed safety requirements concerning the implementation of safety level in accordance with this Act"* [1]. Updates or publication of YVL Guides doesn't change any prior decisions made by STUK, but a separate decision is made after hearing the parties involved.

YVL C.6 *Radiation monitoring at a nuclear facility*, Section 3.7 *Activity monitoring equipment of a laboratory*, paragraph 324, states that *"Under normal operational conditions, equipment shall be available for determining the nuclide-specific activity"*

concentrations of alpha, beta and gamma radiation.".[2] Because of this Fortum needs to have a method for nuclide specific alpha activity measurements, and due to this a separation method for major alpha nuclides was needed for different matrices of Loviisa NPP. The goal of this work was to produce a method suitable for the primary coolant of the plants reactors and possibly for other matrices also.

2 Actinides at the nuclear power plant

Actinides consist of 15 metallic elements in the lowest row of the periodic table, from actinium ($_{89}\text{Ac}$) to lawrencium ($_{103}\text{Lr}$), actinium and lawrencium are in some contexts part of the group 3 elements, but in the broad sense they are considered part of the actinides. Actinides exhibit similar properties and if discussing an actinide in general the marking "An" is used. Even though their properties might be somewhat similar they also show very complex chemistry. For instance plutonium has seven different oxidation states (0, (+II), +III - +VII) and four of those can be present in the same solution. Windorf et al. have reported also the existence of a +II oxidation state for Pu. [3], [4] In context of this work the most important are uranium and the alpha-emitting light transuranium isotopes. They are produced into the fuel by neutron activation, mainly from ^{238}U , this is summarised in figure 1 and later in this text. Transuranium elements contribute greatly to the long-term exposure scenarios due to their long half-lives and high radio toxicity.

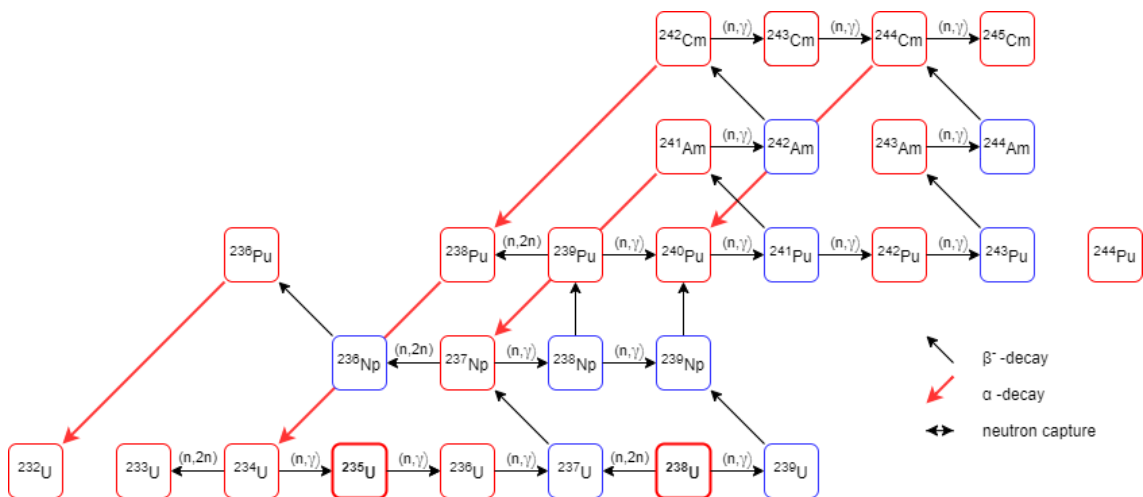


Figure 1: Actinide transmutation and buildup in neutron flux[5]

2.1 Water chemistry in VVER-type primary circuit

In a pressurised water reactor (PWR) normal water (H_2O) is used to transfer the heat generated from the fission reaction of uranium. The water exits the reactor at a temperature of about 300 °C and at a pressure of 123 bar. In these conditions water stays liquid, the conditions are kept below the critical point of water (374 °C and 218 bar), compared to a boiling water reactor (BWR) where water is turned into steam

inside the reactor vessel. In Loviisa the heated water is transferred to six horizontal steam generators where the water of the primary circuit runs in small tubes and heats the water of the secondary circuit. The conditions of the secondary circuit allow the water to boil and steam is generated, which in turn spins the turbine. The cooled primary coolant is then returned to the reactor pressure vessel with the primary coolant pumps (PCPs).

The objective of optimised water chemistry of the primary coolant is to ensure the integrity of the zirconium alloy fuel cladding, minimize the corrosion of other components and control the radiation levels in the primary coolant circuit.

Boric acid is used to regulate the power output of the reactor, because about 20 % of naturally occurring boron is ^{10}B which has a large cross section for neutron adsorption. During normal operation varying the boric acid concentration in the reactor is the primary reactivity control, with the control rod system being the secondary system. The amount of boric acid in the circuit is changed during the production cycle, the amount is dependant of burn-up of the fuel and the desired power level. Ammonia is added to the water to mitigate the effects of radiolysis of water, it is also used to control the potassium buffering capability of the cleaning facility for the primary coolant circuit. Small amounts of hydrazine are used to remove oxygen dissolved into the water during power up. KOH is the main chemical used to control pH_T , which is the high temperature equivalent of pH, at $T = 573 \text{ K} = 300 \text{ }^\circ\text{C}$, this is due to the increase in water autoprotection at high temperatures. [89], [6].

The migration of corrosion products and actinides in the primary circuit can be seen as a system where the corrosion products dissolve and precipitate depending of temperature, pH_T , neutron flux, pressure and the concentrations of O_2 & H_2 . This system is pictured in figure 2. Crud is composed of the corrosion products of the structural materials of the reactor and the primary coolant circuit. It consist mainly of iron with other minor species such as cobalt and nickel. Fretting, foreign objects, crud and reasons related to manufacturing and handling of fuel are large constituents in fuel rod leaking unrelated to the burnup of the fuel. [7], [8]

The target values for pH_T is between 7.2 and 7.3. In low pH_T the corrosion products experience a negative temperature coefficient and the start to precipitate to the surface of the fuel, and activate. In high pH_T the corrosion products start to dissolve from the surfaces. Chloride is kept under $100 \mu\text{g/L}$, Oxygen should be less than $5 \mu\text{g/L}$ and hydrogen should be between $25 - 60 \text{ mL/L}$. K_{tot} is kept on the optimal area

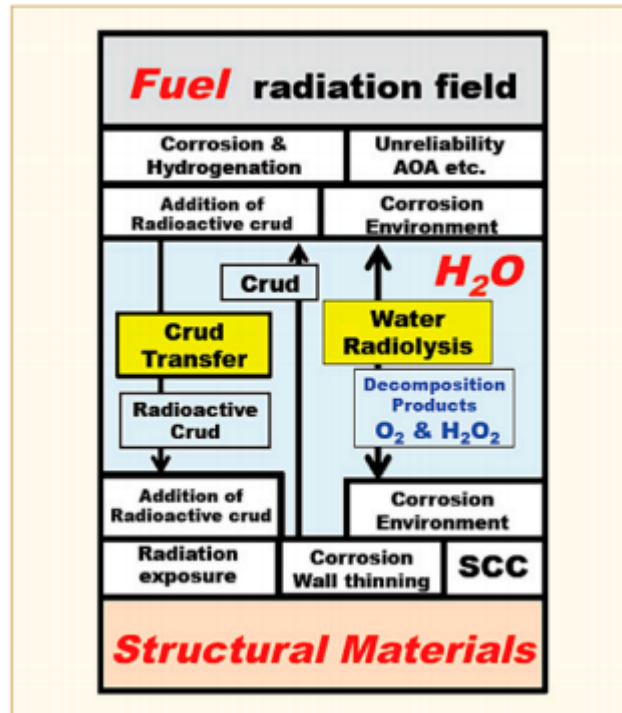


Figure 2: Relations between components in primary circuit [7]

in regards to pHT, which relates to the boric acid concentration, the amount of boric acid in the primary coolant is a safety parameter that depends on the burnup of the fuel and power level of the reactor. In general the amount of boric acid decreases during the production cycle to compensate the burnup of the fissile material. The allowed range of chemistry and activity parameters are defined in the *Operational Limits and Conditions* or OLC, its finnish abbreviation is TTKE that comes from *Turvallisuustekniset käyttöehdot*. OLC is defined for each unit separately. [89], [90] The biggest transients in chemistry happen during power-ups and -downs and generally during the maintenance outage of a plant when the reactor is opened and the water comes to contact with air in the containment.

In acidic solutions boric acid is found mainly in the undissociated form. When pH increases the to about 9 half of the boron present is transferred to the metaborate ($B(OH)_4$) form and in pH over 10 the metaborate ion is prevalent. Highly water soluble polyborate anions ($B_3O_3(OH)_4^-$, $B_4O_6(OH)_4^-$ and $B_5O_6(OH)_4$) are present in pH 6 to 11 [9]

Boric acid corrodes normal steel, but not stainless steel. The high concentration of boric acid in the process waters makes determination of minor components tedious

for it has to be removed from the analyte due to interference caused by it. The amount of boron in primary coolant can vary from almost zero to concentrations of about 15 g/kg. In the fuel pools the boric acid concentration is from 13 - 15 g/kg. In some wastes and storage tanks the amount can be even higher, reaching concentrations in the tens of grams per kilogram of water.

2.2 Actinides in the primary coolant

Before any fuel leaks into the primary circuit there shouldn't be much fission products nor actinides present in the coolant. If there has been a fuel leak in the plants operational history, fission products can be found from the primary circuit, both from the surfaces and the water phase. A source of actinides into the primary coolant comes from the uranium contamination that was present of the fuel cladding's surfaces originating from the manufacture of the fuel assemblies, but modern fuels should not experience this kind of surface contamination. It is estimated that an uranium contamination of approximately 10^{-7} Bq/cm³ results in an ¹³¹I concentration of approximately 10 Bq/L. The possible contamination can then in turn be activated, producing transuranium isotopes that can be dissolved by the coolant.

In the primary circuit there is present residual activity, which is result of past fuel leaks and activation of components. These elements are then either dissolved into the primary coolant or precipitated into the crud. Sudden increases in activity levels in the coolant could indicate a fuel leak, certain readily dissoluble or gaseous fission products are usually the fastest indications of an ongoing fuel leak. The isotopic composition of the leak can be used to determine the age and location the leaking rod. This can be calculated when both the enrichment and composition of each fuel element is tabulated and and the neutron flux distribution within the core is known.

Gamma-emitting nuclides are usually used to determine the burnup of the fuel in case of a fuel leak. Activity ratios of actinides can be also used to determine this. [10] The effect of burnup on actinide activity ratios is presented in figure 3 [5, p. 227]. For fuels used in Loviisa, calculations can be found from the appendix 19 of the Nuclear Materials handbook [91], where the effects of burnup in different types of fuels can be examined. The ²³⁸Pu/^{239,240}Pu ratio was used to determine the burnup of the leaking fuel rod(s) due to its relative indifference to other parameters associated with the fuel rods. Thus the age of the leaking rod could be determined [11]

The amount of actinides present in the primary coolant should be minuscule. Some

considerations of when and how much alpha-activity could be found from the coolant water, with and without an ongoing fuel leak, is presented in the following paragraphs.

A study [11] was performed at Paks NPP on VVER-440 type reactor to assess the actinides in the primary coolant of the reactor. An alpha activity maximum of 5.4 Bq/l was analysed just before opening the RPV (reactor pressure vessel), taken directly from it. Also alpha activities above 1 Bq/l were reported in samples taken directly from the RPV around 100 hours after the shutdown of the reactor. The plant in question had around 300 days of full power production before shutdown and sampling.

During an accident involving some 30 fuel assemblies at Reactor no.3 of Paks NPP the level of actinides (Cm & Pu) was around 10 Bq/L and stayed at that level for a prolonged time. The accident happened in a cleaning tank when crud removal was performed on said fuel assemblies. Inadequate cooling resulted in forming of a gas filled space in the cleaning tank thus resulting in even more damage to the fuel. The INES rating was 3 [serious incident] due to the damage caused to the fuel assemblies. The conditions in the tank differ from the conditions of the primary circuit, but they are considered to be similar enough to make conclusions about activity levels in water after an accident. From the releases an upper limit for a LOCA type incident was determined. This accident was reasoned to surpass design criteria for a LOCA accident. [12], [13]

The relation between both ^{137}Cs and ^{60}Co and alpha active actinides was assessed in a VVER440/230 type reactor with a computer model (OSCAR) in the case of decommissioning, in the reactor coolant system (CVS) and the chemical and volume control system (CVCS). A correlation factors between the surface activities of ^{60}Co and actinides were declared. These are tabulated into table 1. [14] Into the same table a comparison between some actinides and ^{137}Cs is tabulated. These ratios have been determined by Puukko and Jaakkola [15] and they are based on measurements done from the primary coolant, ion exchange resins in the primary coolant and waste resins from a waste tank from Loviisa. The sampling was done both during normal operations and during an ongoing fuel leak. ^{137}Cs to An relation is used due three factors, its relative ease of determination, similar process of creation and it's rather similar chemical behavior to these actinides.

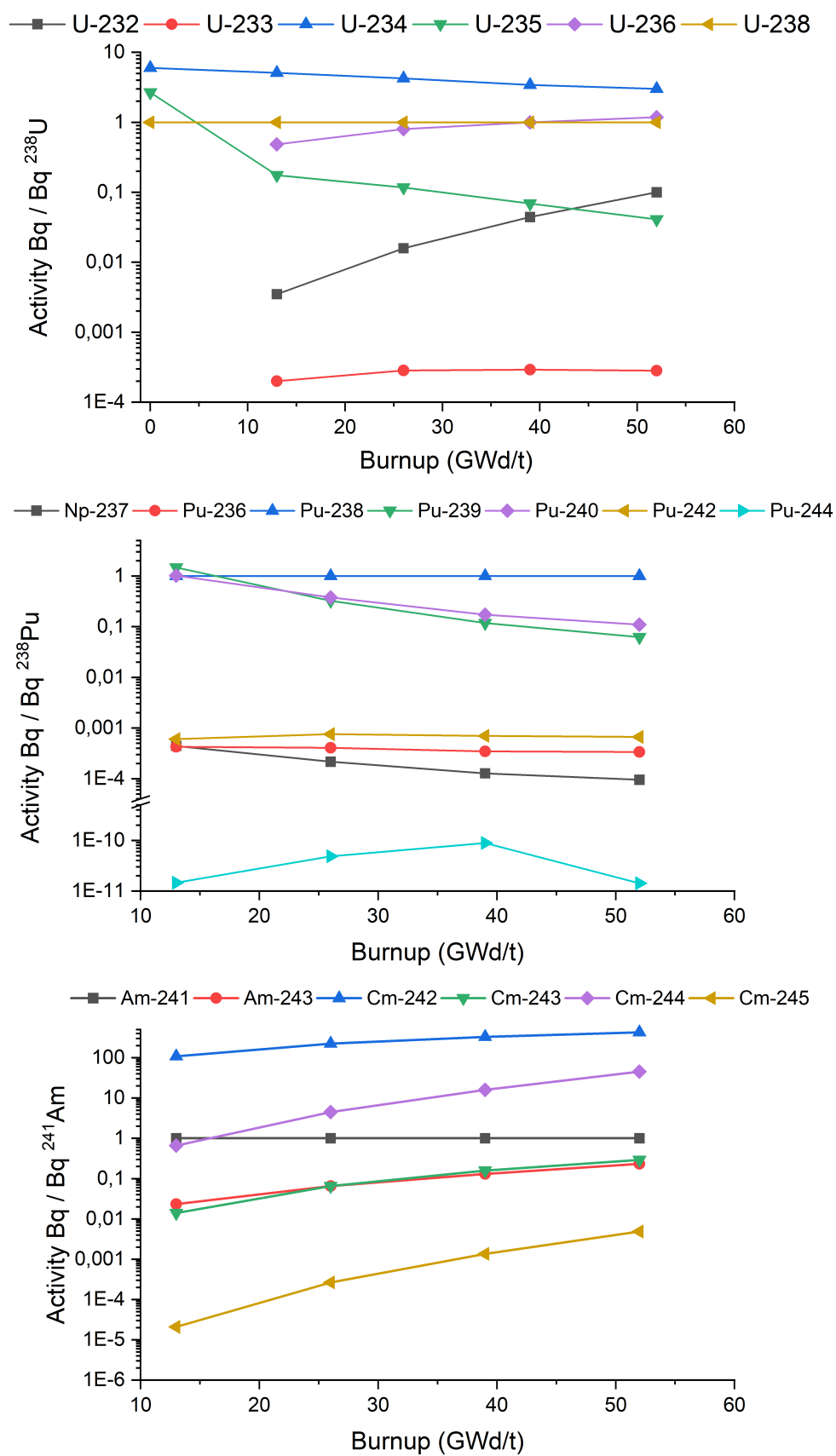


Figure 3: Effect of burnup on activity ratios of uranium, plutonium, americium and curium in PWR fuel [5]

| Nuclide System | Activity / Activity ^{60}Co [14] Primary coolant | Activity / Activity ^{137}Cs [15] Primary coolant and ion exchange resins |
|-----------------------|--------------------------------------------------------------|---------------------------------------------------------------------------------------|
| ^{241}Am | 7.5E-5 | 6.6E-6 |
| ^{235}U | 2.2E-9 | - |
| ^{238}U | 2.2E-8 | - |
| ^{238}Pu | 7.4E-5 | 7.0E-6 |
| ^{239}Pu | 3.0E-5 | - |
| $^{239+240}\text{Pu}$ | 5.2E-5 | 1.0E-5 |
| $^{243+244}\text{Cm}$ | - | 7.6E-6 |
| ^{244}Cm | 5.9E-5 | - |

Table 1: Relations between ^{60}Co , ^{137}Cs and major alpha emitting nuclides in two different cases.

2.3 Actinides in the auxiliary systems and in wastes

Most of the auxiliary systems should be free of actinides originating from the RPV. Most likely places to find them would be the systems used to clean process waters, where there is a possibility for concentration of actinides, either onto resin beds or into the evaporation residue.

Ion exchange resins are used to clean waters and after their capacity is depleted they turn into waste. Resins are interesting as matrices due to the accumulation of metals to them. Ion exchangers which are used to clean the primary coolant tend to be rather radioactive due to this accumulation of impurities both soluble which are captured by the active sites and insoluble crud which is physically retained into the resin bed both due to chemical retention of the soluble species into the active sites of the resin and crud and other particulate matter being physically retained into the ion exchangers. Most of them are based on strong ion exchange resins. Both mixed bed filters composed of both anion and cation exchange resins and singular anion or cation exchanging resins are used depending on the situation. The resins are periodically changed and the old resins are handled as intermediate level waste due to activation and fission product accumulation into the resins.

Waters originating from the process are evaporated to concentrate the activity in the waters and to minimize the amount of radioactivity released into the environment. This is done in the evaporators from which the steam is liquefied, and gathered into a control tank from which it is pumped out to the sea. Before the release a sample is taken from the control tank and measured to ascertain the activity content is

below the release limit. The resulting residue which stays in the evaporator is highly concentrated in boric acid and other nonvolatile components. The residue is gathered separately and processed.

2.4 Actinides and other alpha emitters on surfaces

The radiation protection organisation collects swipe samples from different places around the plant. During the last year a transfer from wet wipes to dry wipes was carried out. The swipes consist of a foldable paper that can be used to protect the round wipe cloth and to make notes about the swipe. The collection of surface samples is described in the standard ISO 7503-2, the standard describes the area of swipe to be 100 cm² e.g. 10 cm x 10 cm area. The devices used to measure contamination indirectly take this into account and they display the activity in Bq/cm². When using the new dry wipes it is assumed that only a certain percentage (<50 %) of the contamination is removed by the wipe. [16]

Swipe samples are usually measured first with a Nutronic NT200 (Nutronic AB, Sweden) swipe sample analyser. It is a lead shielded Ar/CO₂ sealed proportional counter. It has an average efficiency of about 10 to 30 % for alpha energies from 4,2 MeV to 5,6 MeV. Beta efficiency is from 16 to 49 % increasing with growing beta energy. It has a MDA of 0,25 Bq/cm² with a counting time of 10 seconds.[77] Usually samples containing high activities, especially if alpha activity is detected, are brought to the laboratory for more detailed analysis. They are measured with gamma spectrometry and sometimes either with a proportional counter or as a new method, with the iSolo measurement device.

2.5 Alpha emitting radionuclides in air filter samples

Monitoring of the release air is performed with continuous sampling of the air released via the ventilation stack. The sampling is performed with either filtering of aerosols into a glassfiber filter and halogens into an active charcoal cassette. Noble gases are sampled by diverting a part of the sampling air flow into a 4.3 L Marinelli flask and which is in turn measured with gamma spectrometry. Air samples can also be collected with handheld sampling pumps, these samples are taken from spaces where airborne contamination could be present. Both sampling devices use the same aerosol filters, the active charcoal part might be either the cassette mentioned previously or a thin charcoal coated filter.

Air samples collected from the plant should be free of alpha emitting nuclides, apart from radon daughters (NORM), which need to be separated due to their similar alpha energies which cause interference thus enlarging the MDAs of analytes. Airborne alpha-activity should stay low in most accident scenarios. During dismantling of such parts that could have been in contact with uranium crud or the fuel assemblies there is a possibility that due to physical aggravation metal particulates can be introduced to the ventilation system or into the air surrounding the dismantling site. Due to the very high radiotoxicity of actinides in the lungs the amount of actinides should be monitored during such activities, either directly or indirectly to determine the source term of airborne alpha-activity.

3 Actinide analysis from NPP matrices

Both analytical and process scale methods are discussed in this section. First the progress so far is discussed briefly and the classical methods are discussed. After that a brief look is taken into more novel separation and detection methods. Lastly there is a short section on processes involving actinide separations, these are mostly referred to when addressing reprocessing of nuclear waste and in production of certain radioisotopes.

3.1 Analytical actinide separations

Actinide separations can be achieved with liquid-liquid extraction (as done in reprocessing of used fuel), ion exchange, extraction chromatography, precipitation and complexation of either a singular radionuclide or groups of elements, autodeposition (e.g. polonium on silver disks) and other more novel methods specific to a certain radionuclide. Out of these extraction chromatography is the most widely used method in analytical procedures due to the gains in time and reduction in consumption of chemicals, especially strong concentrated acids and organic solvents. Different precipitation and complexation reactions are used in the pretreatment phases to remove interferences

The radiochemical yield is also important to determine with an internal standard, or tracer. The tracers are used with either as a standard addition of a radionuclide already present in the sample or addition of a radionuclide not present. In alpha spectrometry of U, Pu, Am/Cm there are alpha-emitting radionuclides that do not have overlapping peaks with the analytes thus a isotopically different tracer can be used (e.g. ^{232}U , ^{242}Pu and ^{243}Am). The amount of possibly interfering alpha-emitters present both in the sample and tracer are determined by making a tracer free sample and a sample with only the tracer present. [4]

3.2 Extraction chromatography resins

In this section we discuss the resins used in the experimental section and take a look into some other resins of interesting properties. Resins are widely used for transuranium separations, and their performance is excellent, but their use is somewhat tedious and multiple different chemicals are needed to effectively separate and clean the fractions. UTEVA and TEVA are resins manufactured by Triskem/Eichrom and

they are widely used in separating uranium and tetravalent actinides. TRU is used to separate transuranium isotopes. DGA is newer resin also from Eichrom/Triskem. Extraction chromatography is based on the varying affinities of analytes to the stationary phase of the extractant. The ligands of the extractant are bound to the solid phase by dissolving them into a volatile solvent, mixing it with the solid support and then slowly evaporating the solvent. The attraction to the solid phase is described with k' (eq. 1) [4], [17]

$$k' = \frac{V_{max} - v_m}{v_m} \quad (1)$$

where V_{max} is elution volume to peak maximum and V_m is column void volume. The separation factor, SF, between to analytes A and B is described by eq.2

$$SF = \frac{k'_A}{k'_B} \quad (2)$$

The width of the elution band is described by eq. 3

$$SR = \frac{1}{4} \left(1 - \frac{1}{SF}\right) (\sqrt{N_2}) \frac{k'_B}{1 + k'_B} \quad (3)$$

where SF is the separation factor between two analytes, k'_B is k' of the latter analyte and N_B is $\frac{V_{max}^2}{\sigma^2}$ for B where σ is the standard deviation of the elution curve of B. [18]

The uptake into the resin is described with k' . When $k' > 100$ then it can be said that the uptake for an element is significant and k' values between 1 - 50 means weak interaction between target element and the extractant. The k' values of selected resins are presented in appendices 1.1 - 1.4, the tables are gathered from both the works of Horwitz et al. [19]–[22] and the manufacturers datasheets [20], [78]–[81]

3.2.1 UTEVA

UTEVA (Uranium and TEtraValent Actinides) resin is based on the extractant DAAP - diamyl, amyolphosphonate extracts nitrate complexes of actinides from the sample solution. Increasing the concentration of nitric acid present in the sample solution increases the uptake of actinides onto the extraction chromatography resin. For +IV ions of Pu, Th and Np and +VI ion of U an increase in k' can be seen up to $k' = 10^3$ for Pu(IV) 10 M HNO₃. Americium (+III) on the other hand displays

a retention maxima at around 1 - 2 M solution of HNO_3 , and is not retained at any concentration onto UTEVA. Thorium loaded into a column can be separated with 5 M HCl separating it from uranium. Uptake of Th can also be prevented with oxalic acid which forms strong complexes with Th that are not retained by DAAP nor is the retention of hexavalent uranium greatly affected by oxalic acid.

Large amounts of phosphate hinder the retention of tetravalent anions due to phosphate complexes are not readily extracted by DAAP. This can be countered with addition of aluminium (+III) ions which in turn form stronger complexes with phosphates. Using $\text{Al}(\text{NO}_3)_3/\text{HNO}_3$ as the loading solution enhances Np and Th uptake. A 2 mL column of UTEVA has a maximum capacity of around 100 mg of U(VI) but the recommended amount for U(+VI) is around 10 mg /mL. [80]

3.2.2 TEVA

TEVA (TEtraValent Actinides) uses trialkyl, methylammoniumnitrate or chloride as the extractant which is an aliphatic quaternary amine. Because the active extractants are in liquid form they can co-ordinate with target molecules and ions with greater flexibility than those found in rigid strong anion exchange resins. This flexibility results in larger uptakes and a larger viable range for acid concentrations. In nitric acid (2 - 4 M) tetravalent ions Pu, Np and Th ions are extracted with k' of 10^2 of Th(+IV) to 10^5 of Pu(+IV). Am(+III) and Np(+V) are not retained into TEVA at any concentration of HNO_3 and hexavalent uranium is not strongly retained, a difference of about 10^2 in k' can be observed, and even larger difference in retention of Np(+V) and Am(+III). In larger concentrations of nitric acid complexes start to form and the retention of tetravalent actinides is hindered.

In HCl the story is a bit different, hexavalent uranium and tetravalent Np and Pu are retained strongly in 10 M HCl and Th(IV) and Am(III) can be eluted out of the resin. This can be utilised to separate thorium from neptunium and plutonium. Then plutonium and neptunium can be either eluted at the same time with dilute acid or the oxidation state of Pu can be altered by reducing it to Pu(+III) and thus separating Np and Pu. [22], [79]

3.2.3 TRU

TRU is based on the extractant CMPO (octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide) that is dissolved into TBP (tri-n-butyl phosphate). The extracting

phase is then impregnated into an inert backbone composed of a polymer (Amberlite XAD-7). The resin has a density of 0.37 g/mL and a working capacity of 7 mg/mL of Nd and for 2 mg/mL for Am. [82], [23]

Tetravalent actinides are retained exceedingly well into TRU from nitric acid at higher HNO_3 concentrations. Also trivalent iron is retained extremely well in nitric acid concentration exceeding 2 M HNO_3 . Trivalent americium is retained with low k' values ($k' \approx 100$) with HNO_3 concentrations ranging from 2 M to 5 M. With lower and higher concentrations retention of americium is lower. Trivalent plutonium exhibits similar behavior and pentavalent neptunium is not retained at any HNO_3 concentration. Pu,Np,Th(+IV) ions are retained from 7 M HCl and hexavalent uranium is also retained, but with k' values two decades lower. Addition of trivalent aluminium (>0.1 M) ions increases the retention of americium (+III) and presence of trivalent iron (>0.01 M) hinders or inhibits retention of trivalent americium. Uranium and neptunium can be separated from TRU resin using oxalic acid, addition of oxalic acid greatly reduces the retention of neptunium. [82], [23], [24]

3.2.4 DGA

DGA (DiGlycolAmide) resins come in two different variations, normal (N,N,N',N'-tetra-n-octyl diglycolamide, TODGA) or DGA, branched (N,N,N',N'-tetra-2-ethylhexyldiglycolamide TEHDGA). DGA has high affinity to trivalent actinides (and lanthanides + REEs). DGA has a functional capacity of about 15 mg europium per 2 ml column. It has a density of about 0.38g/ml.

DGA can be used to remove many interfering matrix elements using nitric acid. Sodium, potassium, magnesium, and trivalent iron ions are not retained from nitric acid, in higher HCl concentrations iron is retained. Strontium and calcium are retained in nitric acid concentrations between (0.5 M - 5 M). To reduce their matrix effect should sample loading be done with >8 M HNO_3 . DGA can be used to separate yttrium and strontium from each other. Actinides and REEs can then be extracted with dilute hydrochloric acid. Light REEs can be selectively removed before elution of actinides with dilute nitric acid. If analysing matrices with high bismuth concentrations should it be removed before elution of actinides with 9 M HCl. [78], [25]

Vajda et al. have been using DGA to produce separation of U, Np/Th, Pu and

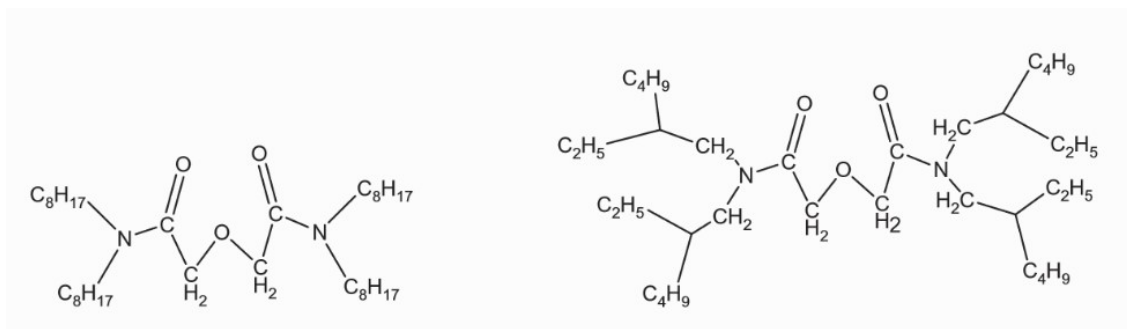


Figure 4: Left TODGA, right TEHDGA

Am/Cm with one column. The procedure involves temperature regulation of the column during elution. Recoveries of over 85 % have been reported for all nuclides of interest. Extremely large loading volumes were reported, 100 to 300 milliliters of 4 M hydrochloric acid. A reducing agent (sodium sulfite, Na_2SO_3) was added to the loading solution to keep the actinides in the desired oxidation state, about 30000 ppm is enough to achieve desired conditions. Also other parameters of the loading solution were optimised. Fe(II) content should be kept between 100 and 1000 ppm to avoid affecting the k' values of U and Th. Calcium content should be minimized to keep the k' factors of Pu and Am high, a maximum of 2000 ppm is desirable. Aluminium(III) and zirconium(IV) don't seem to affect retention of these actinides to DGA. [25], [26]

Actinide partitioning with diglycolamides (DGA) has been studied in for both analytical and reprocessing reasons. Different DGA based based extractant are synthesized around the central diglycolamide-frame, varying the lengths of the alkyl chains, which affects the solubility of the extractant. The main difference between branched (TEHDGA) and non-branched (TODGA) DGA is branching of the alkyl chains, also presented in figure 4. Both of these extractant are commercially available. TODGA is not soluble in water but is dissolved by n-dodecane which is used as an organic phase in liquid-liquid extractions used in reprocessing. TODGA is hydrolytically stable in 3 M HNO_3 for weeks. TODGA is also radiation resistant and it tolerates alpha radiation better than gamma radiation. The resin should not be affected if analytes are retained into the resin and eluated at a later time. [27]

3.2.5 TK201

TK201 is based on a tertiary amine. It has been hardened against radiolysis by adding a minute amount of long chained alcohols to act as radical scavengers. It is considered to have weaker ion pair binding than TEVA, which allows milder conditions for elution of retained species. It is used mainly for Tc/Mo separations, but it also demonstrates affinity to U and Pu at high HCl concentrations, which can be possibly eluted, also Bi and Mo are retained these conditions. Molybdenum is not retained in HNO₃, except in concentrations lower than 0.5 M. In these conditions technetium and rhenium are retained in these conditions, allowing easy separation of Mo and Tc. Rhenium can also be separated from molybdenum using dilute ammonium hydroxide. This can be used in production of radio-pharmaceuticals where separation of Mo/Tc is paramount. Copper, nickel and zinc can also be separated from each other using TK201-resin which can be enhanced with use of Triskem copper-resin. [81], [28]

3.2.6 Actinide Resin

Actinide Resin is based on the DIPEX extractant (P,P'-di(2-ethylhexyl)methanedi-phosphonic acid). Also known as AC Resin or DIPEXTM. This resin has very high k' values for actinides in low HCl concentrations decreasing with increasing acid concentration. The reported capacity for Actinide Resin varies with the charge of the ions, for uranium(+VI) it is 145 mg U/g resin, for Th(IV) it is 86 mg/g, for Nd(III) it is 45 mg/g and lower for divalent ions.

A method utilizing the Actinide Resin, is presented by its manufacturer Eichrom. This method utilises a free form of the resin which is added straight into the sample liquid, it binds most of the actinides into itself. The resin is left into the sample liquid for 4 - 18 hours after which it is removed from the sample solution with filtration onto a 0.45 micron filter. Then the resin is washed, dried and transferred into a liquid scintillation vial with a minimal amount of 0.5 M HCl. LSC-cocktail is then added and the sample counted. [20] Gross actinide alpha measurements can be performed in this way within hours and detection limits of around 30 mBq/L have been reported. 0.3 g of Actinide Resin is added to a water sample of 100 mL and mixed for 4 hours. Then the resin is filtered out, or the whole filter is transferred into a vial, LSC cocktail is added and the sample is counted for 4 hours. The organic matrix of the LSC both dissolves the extractant from the resin and

turns the filter translucent. The resin then descends to the bottom of the vial, while actinides extracted by DIPEX spread evenly into the LSC enabling LSC counting. [83], [29]

3.3 Recent progress on separation and detection methods

In this part a review is presented of recent progress in separation and detection of actinides, with an emphasis on analytical separations and other methods relevant to NPP operations.

3.3.1 Commercial resin tweaks and other tricks

Plutonium and neptunium can be separated from interfering components with either AGMP-1 (Bio-Rad company), an anion exchange resin, or TEVA, extraction chromatography resin. Interference from ^{238}U is major interference when analysing both ^{237}Np and ^{239}Pu with ICP-MS due to tailing and formation of the UH^+ ion. TEVA-resin showed a better decontamination factor for Pu and Np from U than the anion exchange resins. [30]

Using a stacked TEVA-UTEVA-DGA system can increase the decontamination factor greatly. The procedure involved firstly loading the sample into a TEVA cartridge from which Ca, Fe, REEs could be eluted with 10 mL of 3 M nitric acid. Then uranium, lead, thallium and platinum were removed with 40 mL of 1 M nitric acid. Lastly thorium, bismuth and hafnium were removed with 10 mL of hydrochloric acid. Then preconditioned (10 ml 3 M HNO_3) UTEVA and DGA columns were connected beneath the TEVA cartridge. Plutonium was then eluted with 3 M HNO_3 - 0.1 M ascorbic acid - 0.02 M Fe^{2+} . This reduced the plutonium present in the TEVA cartridge from Pu(+IV) to Pu(+III). Trivalent plutonium passes thru the UTEVA cartridge, which traps uranium, and is retained in DGA cartridge. To further clean the plutonium partition the DGA column was rinsed with 30 mL 0.1 M nitric acid and plutonium was eluted with (0.5 M HCl - 0.1 M hydroxylamine hydrochloride ($\text{NH}_2\text{OH} - \text{HCl}$)). [31]

During the course of the work a need for some replacement chemicals rose due to difficulties in procuring them. It has been determined that plutonium can be easily extracted from column and there is no need for reduction of plutonium(IV) to Pu(+III) when eluting it from a TEVA column with dilute acid. [32] This was tested with some samples both, either by not using titanium(III)chloride or reduc-

ing the amount, in the elution of plutonium, no significant difference in plutonium recovery was detected. Another possibility is to use hydroxylamine hydrochloride to eluate plutonium from TEVA. [30] TiCl_3 is also used as a reduction agent to lower the oxidation state of uranium (VI) to U (IV) to enable coprecipitation of uranium with neodymium fluoride. At least these chemicals have been used for uranium reduction: Tin(II) chloride, titanium(III) salts, sodium hyposulfite ($\text{Na}_2\text{S}_2\text{O}_3$), iron(II) with fluorides present, Rongalite, lead and Jones reductors (Jones reductor produces trivalent uranium ions), electrolytic reduction, zinc amalgams. [33], [34] A study involving production of an aqueous pentavalent uranium species is described by Faizova et al. [35]. The uranium complex $[\text{U}^{VI}\text{O}_2(\text{dpaea})]$ is rapidly reduced to a pentavalent state by sodium hyposulfite, which in turn is then converted over time span of days to an insoluble U^{IV} oxo-hydroxo complex. Uranium can be reduced to tetravalent state with sodium hydrosulfite $[\text{Na}_2^+[\text{S}_2\text{O}_4]^{2-}]$ in alkaline EDTA solution. The solution should be alkaline to prevent decomposition of the hydrosulfite ion and sulfur precipitation. Ferrous iron partially reduces uranium and ascorbic acid can be used to reduce uranium in the presence of iron. [36] Small amounts of Mohr's salt can also be used to reduce actinides. [26]

3.3.2 Pretreatment and sample handling

Efforts to omit hydrofluoric acid in the pretreatment of different matrices was discussed in multiple studies. In concrete analysis HF is used to remove silica that interferes with the subsequent separation steps and traps part of the analytes in undissolvable form. A common fusion technique is using NaOH in Zr crucibles with an additional step using HF to remove silica. HF was also reported to be used in pretreating radioactive slurries for Si removal. HF was replaced with a combination of first performing a lithium borate fusion and afterwards flocculating silicon colloids with polyethylene glycol. The process involved first ashing the sample at 900 and fusion at 1100 °C. [37]

An automated sampling and separation system using parts commercially available was presented by Higginson et al. [38] The authors claim that using this system they could reduce both sample size and waste generated. The method is intended for small highly radioactive samples. Polypropylene filters used to remove solid particles from a pool-type research reactor water were analysed to assess their radionuclide inventory. The equipment used was almost identical to the equipment used in the experimental section of this work. The filters, approximately 50 cm in length were

cut evenly so that five 2 cm slices were obtained from the filter. The slices were then cut in half and the other half was soaked with alcohol and burned in a porcelain crucible. The remaining material was calcined for a day at 350 ° Celsius. The ash was digested with three times with a mixture of HNO₃ and HCl (aqua regia) (3 x 20 mL) which was evaporated to dryness (250 °C) between the digestions. Additional digestion was performed with 10 mL of conc. HNO₃ and 10 mL HCl₄O. This was also evaporated and the remainder was dissolved into conc. nitric acid that was added in batches accompanied with a small amount of H₂O₂ which is added to remove any remaining HCl₄O. This was again evaporated and the remainder was dissolved into 20 mL of 8 M HNO₃. Gamma-analysis was performed on a diluted subsample. First plutonium was reported to be separated with 1 x 2 Dowex resin. The fractions containing uranium, americium and curium and possibly plutonium were separated with the help of the Eichrom method discussed in the experimental section. [39], [84]

A pretreatment scheme for soil and sediment is presented by Vajda et al. [26] The sample can be destroyed for analysis with a fusion with sodium hydroxide. The actinides are then co-precipitated to remove interfering silica, iron and calcium ions. Some actinide oxides and minerals containing actinides are not completely digested in mixtures of HF, HNO₃, HClO₄ and they need filtration before analysis to remove the solids left after the acid digestion. Lithium borate fusion was used to destroy completely samples up to 4g. The procedure involved firstly muffling the sample in an oven (650 °C) for 4 hours to remove all organic matter, then tracers and lithium borates were added to the sample and it was dried in an oven, the dried sample was then fused in a platinum crucible at 1050 °C for about 20 minutes, the resulting liquid was then directly poured into a teflon beaker with MilliQ-water. No residue was found from the solution. The separation of actinides was done with UTEVA - TRU method (ACW03 - VBS - v1.6) and neodymium coprecipitation. Acid digestion resulted in smaller activities determined and it was suggested that significant amounts of analytes would remain in the residue and affect the analysis. [40], [41]

Large amounts of seawater can be preconcentrated with Actinide Resin for actinides, within hours. The procedure involves first filtration and acidification of the sample to pH 1. The sample is then eluted thru multiple parallel Actinide Resin cartridges, the authors used up to 8 in parallel thus achieving a total flow rate of 400 mL/min, with the optimal flow rate per column being 50 mL/min. The columns were then

first separated from the sampling apparatus, the resin removed from the cartridges and the resin was then dry ashed in 600 °C. The resulting ash was dissolved into conc. nitric acid and sonicated and then transferred to a microwave assisted digestion system and digested in 220 °C, while digestion in 200 °C didn't result in reproducible results. The authors discovered that using an alkaline fusion process is not possible for Actinide Resin due to the large amounts of P and C in the sample that caused deterioration of the Pt crucible used in the process. Uranium recoveries reported were over 80 % even for large amounts of water and decontamination factors for interfering elements were high. [42]

A procedure to analyse environmental rock samples are analysed with a stacked TEVA / DGA system. The sample (1g of granite) is fused with NaOH in a Zr crucible for about 15 minutes in 600 °C and then dissolved into water. Actinides are separated with a phosphate coprecipitation to separate the liquid phase from the remaining solids. The liquid phase is discarded and the solid phase is then dissolved into dilute HCl and excess of HF is added to remove interfering silicates and alumina. This results in a fluoride precipitate which is again separated from the supernate. The sample is again dissolved with 3M HNO₃ - 0.25M H₃BO₃, the boric acid complexes the fluoride ion and thus the precipitate is dissolved. A load solution is prepared with adding Al(NO₃)₃ and resulting in a 3M HNO₃ / 0.1M Al(NO₃)₃ solution. Additional chemicals are used to adjust the valence of the analytes. Then the columns are loaded, rinsed and separated. Most part of Th, Np and Pu are retained into the TEVA cartridge and Am,Cm are retained into DGA. The TEVA cartridge is eluted as described in the experimental section (4.2.1) and Am/Cm are eluted as follows from the DGA column. First Ca, lanthanides and Th are eluted with 3M HCl (Ca), 0,1M HNO₃ (La, Ca), 0.05M HNO₃ (La) and 3M HNO₃ - 0.25M HF (Th) Then Am/Cm is eluted with 0.25M HCl. An additional rare earth removal can be performed from the eluant with a TEVA cartridge, this involves redissolving the analyte into 4M NH₄SCN and then loading into TEVA, rinsing with 1.5M NH₄SCN and then stripping the Am/Cm fraction with 1M HCl. The authors claim that the method is fast and efficient with high yields for both Am and Pu. [43]

3.3.3 Novel separation methods

Nanoparticles made of MnFe₂O₄ were investigated in removal of Th(IV) and U(VI) from water. This material has some interesting properties, it is magnetic, so it can

be extracted from the media using magnets, the absorption maximum was reached within hours and U and Th could be extracted from it using HCl (recoveries over 92 % and 96 % respectively), separation of the fractions could be done with Na_2CO_3 which removed some 80 % U and only <10 % Th from the solution. [44]

MnO_2 embedded fibers were reported to be used as absorbents for Ra, Th and Be from seawater. It was reported that a sample size over 1 cubic meter was required for determination of cosmogenic ^7Be . The sample was passed thru the fibres. Alpha analysis was performed on ashed samples, after which the samples were placed in epoxy resin for gamma spectrometry. [45] Another study discussed synthesis and usage of ACPAN fibers (modified polyacrylonitrile) to treat radioactive waste waters, the study focused on removal of uranium from the water, the fibers removed hexavalent uranyl ions with a maximum adsorption capacity of 160 mg/g. The adsorption of interfering elements was reported to be much lower than U(VI) and the fibers could be used with a decent performance for multiple adsorption and desorption cycles. [46] Thorium extraction with a primary amine based N1923 levestrel resin in a micro column was tested with iron ore from a Chinese mine. A decompression device was reported to be used as the flow rate controlling measure. The authors reported that the resin could be used 12 times before significant drop in performance. [47]

Ye et al. reported uranium adsorption on Dibutyl-imide chelating resin. The characteristics of the resin were analysed and described. This resin has a rather large uptake of uranium from an aqueous solution in neutral pH also uranium can be eluted enabling the reuse of the resin. The porous resin exhibited an uptake of 76 % from an uranium solution containing 0.1g/L of hexavalent uranium. [48]

Ionic liquids have been studied recently for many different uses, and their use in liquid-liquid extraction has been also investigated. ILs could be used to extract heavy metals from water and thus it was thought to test their capability to remove U, Th [49] and NORM nuclides from the U series. [50], [51]. Uranium and polonium were extracted with sufficient efficiency. Extraction of the other nuclides was much more dependant on pH and time, and the efficiencies were rather low for the other nuclides. Some of the ILs used in the extraction could be reused due to favorable back-extraction properties. [52]

3.3.4 Other novel detection methods

A replacement for liquid scintillation cocktail for gross alpha measurements is proposed by Janda and Nemec, a powdered form of cerium doped yttrium aluminate perovskite (YAlO_3) or YAP:Ce. Instead of adding liquid scintillation cocktail into the sample, a small amount of powdered YAP:Ce (100 mg) was added. Direct measurement of this matrix proved difficult, but after decanting the matrix (urine) and measuring only the dried powder residue a significant increase in counting efficiency was observed. Adding a small amount of ammonia increased counting efficiency even more. Actinides seem to be incorporated onto the surfaces of the YAP:Ce powder, thus removing them from the urine phase. [53]

A method for to detect the presence of plutonium and uranium is proposed by Riddle and Demmer. [54] This method (Colorimetric Detection Method for Actinides (CoDeAc)) is based on a change in the color of the analyte and can be used to verify presence of these elements at a certain level. They demonstrated in this proof of concept that on both solutions and wipes the change in colour could be observed if actinides were present.

Actinide borates and especially their solid forms are being studied. Molten boric acid has been used as a reactive flux in synthesis of these new borates. These new compositions have been argued to perhaps give new insights to separation methods and their chemistry could have a role to play in disposal of radioactive waste in geological repositories where boron compounds are present. [55]

Alpha spectrometry can also be applied to liquid evaporation residue without separation. A sample of water is acidified with nitric acid yielding an about 10 % nitric acid solution, this converts metal chlorides to metal nitrates. Then the sample is evaporated. There is a possibility of peak resolution deteriorating due to nitrates gathering moisture from the surrounding air, to counter this, the planchets holding the evaporation residue were flamed until a red colour could be observed on the metal. This process removes humidity and converts the metal nitrates to oxides. The samples were then weighted and measured with a grid ionisation chamber. Flaming for 5 to 10 minutes was required to minimize the effect of humidity [56]

3.4 Short look into recent progress on separation methods used in reprocessing of nuclear fuel

Although these processes are intended for large scale reprocessing of nuclear waste, the chemicals and extracting reactions are the same also on small scale. The research can be used for troubleshooting and deeper understanding of the underlying processes and interference's. Usually the analytical procedures rely on extraction chromatography where the extractant is suspended in a liquid on a resin surface. The larger processes emit the resin to bind the extractant in place and the extractions are performed with liquid-liquid extraction between two different liquids, either organic - organic or water - organic phases. In these processes the extractant is usually mixed into the organic phase thus enabling the reuse of the extractants because they can be recycled within the process. This reduces the amount of solid waste created. [23]

There are research done also on solid extraction media similar to the extraction chromatographic methods used in the analytical procedures. The solids emit the organic solvent that has a tendency to degrade due to both radiolytic and chemical damage and wear. The kinetics of the adsorption reactions are also usually faster in solid media. The solids also enable a wider range of extractants to be used because they don't need to be soluble into the organic phase. The solid extractants also tend to create a lot less waste compared to the waste generated in a liquid-liquid extraction system. The extractions are simpler, faster and more cost effective. There is also a possibility to use the extraction media straight as a waste or transmutation matrix. Most of the materials and procedures are derived from analytical methods and materials. [57]

There are many different media tested for solid-phase materials in extraction. The base materials include polymer resins and membranes, porous silica, metal oxides, clays, carbon-based materials, and magnetic nano-particles. Apart from the batch experiments little research has been performed on larger scale systems. [57]

Separation of actinides from processes is mainly done when fuel is reprocessed. The result of the reprocessing can be either pure elements or mixed oxide fuel (MOX). Depending on the desired end product minor actinides (MA's) are usually removed from the matrix. There are cases where they could be left in or concentrated into a separate fraction. These cases usually involve the desire to use the neutron flux of the reactor to either make them undergo fission or transmute them into isotopes

that have shorter half-lives. ^{241}Am is the most contributing element in the 100 year time span and transmuting it can lead to significant reduction of radio toxicity of minor actinides in this time frame. Also the use of MA's as burnable poison in the fuel cycle could be used to reduce the amount of boron and gadolinium needed to control the reactor. [58]

Reprocessing nuclear fuel removes mainly uranium and plutonium from the resulting liquid. The resulting high-level liquid waste (HLLW) contains the fission products and MA's. Separation of rather radiotoxic MA's from lanthanides is also investigated heavily in countries that have reprocessed nuclear fuel. Most of the fission products are less radiotoxic or they have shorter half-lives than most of the MA's, also some lanthanides have very large neutron cross-sections causing them to act as neutron poisons. Thus it is desirable in this context to partition MA's from HLLW and then transmute these MA's to shorter lived fission products in fast reactors or particle accelerators.[59]

PyTri-Diol (2,6-bis[1-(propan-1-ol)-1,2,3-triazol-4-yl] pyridine) has been used to separate Am(III) from Eu(III) from acidic bis(2-ethylhexyl)phosphoric acid (HDEHP). PyTri-Diol is designed to be a selective agent to complexate trivalent americium into nitric acid. A $SF_{Eu/Am}$ of about 900 was reported in liquids up to 0.5 M HNO_3 . PyTri-Diol can also be used to remove other lanthanides from americium containing solutions. It was primarily designed to be used in the TALSPEAK -process. [60]

4 Experimental

The experimental section consist of several parts. First the equipment and methods tested are presented. Then a word about matrix effects on the separation schemes. A brief but important look is made into chemicals used and how the produced wastes should be discarded. Lastly the validation of the chosen methods is presented.

4.1 Equipment

Prepared counting samples were measured with the Canberra Alpha Analyst measurement system (4x2 chambers) utilizing 450 mm² PIPS detectors (Canberra GmbH, Germany) operated with the Alpha - APEX counting software. [85], [86], [92] Some samples were also analysed with iSolo alpha/beta counting system (Canberra GmbH, Germany) which is a portable counter for planar samples, e.g. swipes and filters, that utilizes a larger PIPS detector in ambient atmosphere with relatively short distance between sample and detector. The results are discussed in section 4.2.5

Alpha spectrometry is based on resolving the energy of the alpha particle formed in the decay process. The energy of an alpha particle is somewhat linked to the stability of the parent nuclide, longer half-life causes a lower alpha energy. The samples used in alpha spectrometry need to be near massless to defer degrading of energy resolution which happens in energy loss to sample media, other interfering subjects might be background from the daughter nuclides of the analytes deposited into the detector or degradation of the vacuum resulting in alpha particle energy loss due to air. [61], [62]

The speed of the separation is controlled with the vacuum box system (VBS) (Eichrom ltd. USA / Triskem, Belgium) that can be used to adjust the pressure difference over the separation columns. Different methods have been reported: A constant pressure difference (5 inHg - 30 inHg) or a semi constant flow rate achieved by adjusting the vacuum.

4.2 Separation methods used in experiments

4.2.1 Uranium, Plutonium, Americium and Curium from water samples

The method provided by Eichrom (Eichrom ACW16VBS)[84] uses two or three different resins, they are TEVA, TRU, and optionally DGA, in series for the separation,

depending on if neptunium and thorium are being analysed. The method is based on research by Horwitz et al. The separation scheme is presented in appendix 2. [24], [63]

A sample of 1 liter or less was acidified and the actinides were co-precipitated with calcium phosphate. The resulting precipitate was in turn dissolved into acid solution from which U, Pu and Am/Cm were retained into stacked TEVA and TRU cartridges. The analytes were then extracted from the separated columns into fractions from which the actinides were in turn coprecipitated with NdF_3 . The coprecipitated subsamples were then counted with an alpha spectrometer to determine yield and activity of analytes. [87] The separations and precipitations were aided with the vacuum box system (VBS), which is seen in figure 5. Inside the box the holder for 50 ml centrifuge tubes can be seen. The bypass valve can be seen under the pressure gauge on the right. The yellow outer tips with the white inner tips can be also seen. There is one set of UTEVA/TRU cartridges installed with a 20 mL reservoir. The separate tubes can be replaced with a larger container to collect all of the liquids passed thru the system but if the system fails this results in mixing of all the sample liquids.

For preconcentration of water samples, the sample is acidified with addition of 5 mL of conc. HNO_3 and calcium nitrate is added to the liquid. The sample is then heated and phenolphthalein indicator is added. Di-ammonium hydrogen phosphate is added and the pH is risen with ammonium hydroxide, until the pink colour of phenolphthalein stays in the solution and precipitation starts. The sample is then heated for a while and cooled to room temperature, cooling can be accelerated using a cold water bath. The liquid phase can then be decanted and discarded. It was noticed that if the precipitate is very light, the use of centrifuge is recommended to ensure proper retrieval of the precipitate, this also eased the decantation of the liquid phase. The precipitate is then washed to remove traces of ammonium hydroxide and the indicator, after washing the precipitate is dissolved into a minimum amount of conc. nitric acid. This is in turn evaporated to dryness.

After pretreating samples a precipitate containing metals in their nitrate forms is reached. This precipitate is dissolved into a mixture of 3 M HNO_3 and 1 M $\text{Al}(\text{NO}_3)_3$. Aluminium is present in the solution to increase the retention of americium into the TRU resin. Sulfamic acid is added to reduce all plutonium to Pu (III), after which ascorbic acid is added to reduce Fe(III) to Fe(II). Trivalent iron interferes with americium ja Pu (III) retention on TRU resin. Sodium nitrite is added to adjust

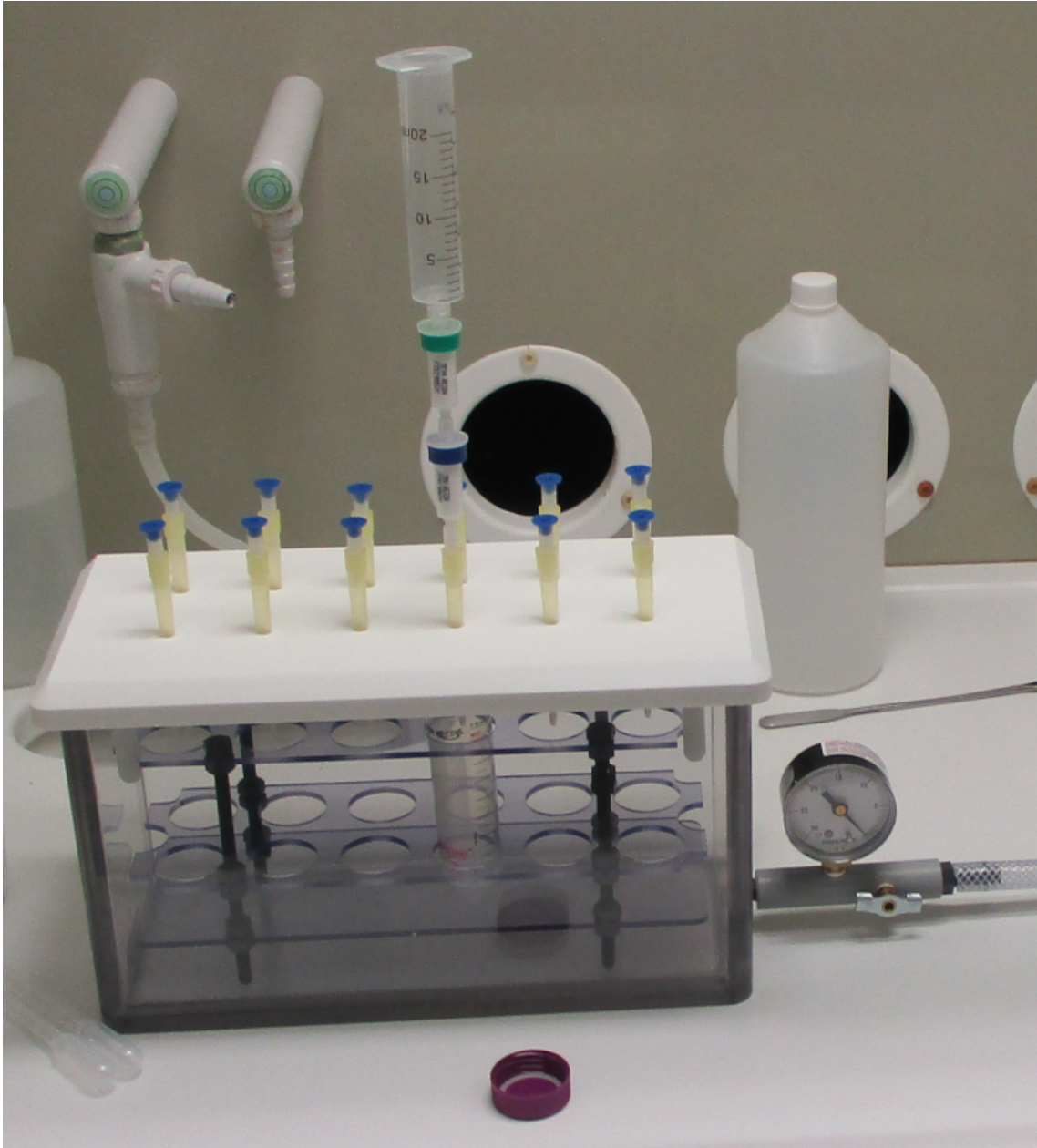


Figure 5: Vacuum box with 12 sample positions

the oxidation state of plutonium to Pu(IV).

Before loading of the sample solution the TEVA and TRU cartridges are pretreated with 5 mL of 3 M nitric acid. The samples are then loaded into the stacked TEVA-TRU system where the TEVA cartridge is stacked on top of the TRU cartridge. TEVA retains Pu, Np and Th in the conditions used and TRU retains americium, curium and uranium, the small amount of thorium that passes through the TEVA column is retained also in TRU. After loading the sample solution the beakers and the feed tank is washed with 3 + 5 milliliters of 3 M nitric acid. After the wash the columns are separated.

TEVA column is washed with 10 mL of 3 M nitric acid and thorium is removed with 15 mL of 9 M hydrochloric acid. Then plutonium is eluted with 0.1 M HCl/0.05 M HF/0.03 M TiCl₃. Titanium(III)chloride is used to reduce plutonium to +III. Retention of tetravalent plutonium on TEVA is also greatly reduced with decreasing acid concentration. If reduction is needed NH₄I can be also used, but this generates a precipitate that needs to be removed before a counting sample can be prepared. Dilute hydroxylamine hydrochloride could be also used for elution of Pu from TEVA-cartridge. [79], [24], [32], [64] Americium and curium are eluted from the TRU column using 15 mL of 4 M hydrochloric acid. The residual thorium passed through the TEVA column is removed into waste by eluting it with 12 milliliters of 4 M HCl/ 0.2 M HF solution. Then uranium can be eluted with 20 milliliters of 0.1 M ammonium bioxalate.

A similar sequential process, without the VBS, is described by Toma et al. [65] where yields for Am, Pu, U are between 95 % and 61 % and the MDA reported were around 0.2 to 0.6 mBq/sample with a measurement time of 100000 seconds or about 27.8 hours.

4.2.2 Sample preparation via precipitation (Eichorn SPA01)

Sample preparation is straightforward, neodymium chloride and hydrofluoric acid are added to the end-product of the separation fractions. The vials are put into a refrigerator for about an hour, after which the resulting NdF₃ precipitate is filtered onto a 0.1 μ m filter, either using disposable funnels with the vacuum box, or a syringe to push/pull the sample liquid through the filter. The sample is near weightless, so no broadening of the alpha peaks should happen.

Possible interferences come from lanthanides that follow their similar actinide species

and transition metals that precipitate with the NdF_3 causing peak broadening due to thickening of the sample.

The tetravalent uranium ion is precipitated with NdF_3 and the hexavalent ion stays in the liquid form as uranyl. To ensure that uranium is present as the tetravalent ion in the solution a reducing chemical needs to be added to reduce the soluble hexavalent uranium. In this method titanium (III) chloride is used to reduce uranium before addition of hydrofluoric acid. [36], [87]. Small amounts (few crystals) of both iron (II) chloride and Mohr's salt were used as substitutes for titanium (III) chloride in some samples. The amount used was low enough that no adverse peak broadening was detected.

4.2.3 Preparation of self-cleaning ^{232}U Tracer

Eichrom has published a procedure to remove the thorium daughter of ^{232}U from the uranium tracer solution. This was utilized to craft an uranium tracer with a smaller activity concentration of dissolved thorium for the validation experiments. The procedure involves coprecipitation of thorium with barium sulfate.

The tracer solution was produced by weighing 4.5 grams of K_2SO_4 and 2 grams of Na_2SO_4 and adding the ^{232}U stock solution into the salts. Then 2 milliliters of concentrated sulfuric acid was added and the sample was heated until a thick melt was formed and the generation of fumes was reduced significantly. The melt was then cooled and dissolved into 25 mL of milli-Q water and 3.2 mL of concentrated nitric acid. When the solid had dissolved 300 microliters of 30 % H_2O_2 was added and carefully mixed. Then 30 milligrams of BaCl_2 was dissolved into 2 mL of milli-Q water and the solution was added dropwise into the other solution. The solution was heated and mixed at the same time, the formation of barium sulfate could be observed in the tracer solution. The suspension was cooled and diluted to 100 mL in a volumetric flask. For storage and use the tracer was transferred into a plastic bottle.

The tracer is prepared by mixing the suspension in the plastic bottle and taking a small aliquot, about 0.1 mL larger than the desired amount, from the solution. The suspension is then centrifuged to separate the precipitating BaSO_4 and Th from the liquid phase containing uranium. The desired amount of tracer is then taken from the the liquid phase, leaving the precipitate and a small amount of liquid to the bottom of the sample vial. The tracer solution was centrifuged in a 5 mL vial

with a cap for about 5 minutes at 4000 rpm. The tracer was used with samples that needed larger amounts of tracer to minimize the interference to other tracer nuclides from ^{232}U and its daughter nuclides. No interfering thorium contamination was detected in the samples produced with this method. [66], [88]

4.2.4 DGA-methods

A separation method of U(VI), Am(III) and Pu(IV) utilizing DGA is reported by Horwitz, McAlister, Bond and Barrans [19], it consists of the following procedure:

- Load sample (3.0 M HNO_3 + 0.1 M NaNO_2 + (250 mg Fe(III)) (10 mL)
- Rinse 3 M HNO_3 (10 mL)
- Elute U: 0.1 M HNO_3 + 0.03 M NaNO_2 (20 mL)
- Elute Am: 0.1 M HCl + 0.03 M NaNO_2 (20 mL)
- Elute Pu: 0.10 M Ammonium oxalate (20 mL)

This procedure is fast, and the chemicals used in this separation are readily available in most laboratories. The separation can be performed in a couple of hours, if there is no need to preconcentrate the sample, if preconcentration is needed it adds approximately two hours more to the analysis time. Iron (III) content affects the recovery of uranium, in low iron contents the recovery should be larger. With iron (III) content in the 25 mg/mL range U recovery was reported to be around 82 % and over 90 % in Fe(III) contents of about 10 mg/mL. [19]

Different methods have been designed at the Paks NPP using DGA-resin. Multiple different matrices have been analysed using a couple different methods. Also a quick method for gross alpha has been studied. [25], [67]

A method to separate actinides from evaporation waste was proposed [25], for waste solutions a more throughout pretreatment phase is needed. A sample of 100 mL was evaporated to dryness. After the first evaporation a series of acid digestion steps were performed with evaporation of the liquid phase in between. The scheme was: 2 x 30 mL 65 % HNO_3 , 30 mL 65 % HNO_3 + 5 mL 30 % H_2O_2 , 30 mL 37 % HCl . Lastly the sample was dissolved into 200 mL of 1 M HNO_3 and filtered thru a 0,45 μm filter.

Iron was reduced by adding a few mL of 70 % hydrazine and heating for about 30 mins. After a rhodanide test that showed that all of Fe(III) was reduced to Fe(II), 1 g of Mohr's salt was added and pH was adjusted to 8 with NH_3 . After an hour of continued stirring and heating the sample was cooled. The resulting precipitate was removed from the liquid by filtering. The filtrate was dissolved using a miniscule amount of 37 % HCl. HCl was evaporated at low temperature and the resulting precipitate was in turn dissolved into a solution of 0.5 M HCl (15 mL). One gram of Na_2SO_3 was added and again the iron reduction was checked with a rhodanide test and if necessary more Na_2SO_3 is added. The acidity was adjusted to 4 M with conc. HCl for loading into a DGA column.

The separation on column after loading the solution consisted of removal of Ca and Fe, with 4 M HCl [20 mL] and 4 M HNO_3 [10 mL] respectively, after which uranium was stripped as U(VI) using 20mL of 0.5 M HNO_3 . Then the column was rinsed using 5 mL of 0.5 M HNO_3 . Reducing conditions were then achieved using 4 M HCl and 0.05 M Fe(II) [15 mL]. Then Th and Np(IV) could be stripped using 25 mL with a mixture consisting of: 0.5 M HNO_3 , 0.05 M oxalic acid, 0.01 M Fe(II). The column was rinsed for the plutonium strip using 5 mL of the previous solution without Fe(II). Pu stripping was performed using 20 mL of 0.5 M HNO_3 , 0.05 M oxalic acid and 0.1 M $\text{K}_2\text{S}_2\text{O}_8$. Again the column was rinsed with the same solution as before and Am was stripped using 0.5 M HCl. The separations were performed at elevated temperatures between 25 and 40 °C. This was performed by the authors to achieve better and more reproducible results. [25]

4.2.5 Rapid gross-alpha with alpha spectrometry

Tests were performed to assess the method presented by Vajda. [68] This method for fast gross alpha determination is based on DGA. Initially two different approaches were assessed. One in which the analyte was mixed with the resin and stirred and a second based on normal columns of DGA. In the first method the resin was added to a 200 ml plastic beaker and mixed with tracers in a solution containing 4 M HCl and Na_2SO_3 . The second sample was loaded into a column by adding tracers directly into the loading solution (4 M HCl / Na_2SO_3).

After stirring overnight the resin was removed from the solution and reloaded into a column, Uranium and transuranium elements were extracted from both of the resins with a solution containing 0.5 M HCl and 0.5 M oxalic acid. Vajda et al. reported that uranium, plutonium, americium and curium should be eluted from the resin.

Afterwards counting samples were produced with neodymium coprecipitation, as described before. Both the effluent and eluate were prepared into measurement samples.

The samples were then counted for 10 minutes on an iSolo alpha/beta counter (Mirion Technologies (Canberra), Inc) to assess the distribution of alpha activities between the partitions. iSolo utilizes a large PIPS detector (2000 mm²) in ambient pressure. The counting conditions are not favorable for alpha spectrometry, broadening the peaks due to energy loss of the alpha particles into the air and less than favorable angle of impact for alphas emitted towards the edges of the detector. Even in these situations the system produces a decent alpha/beta spectrum that can be used to estimate the nuclides present in a gross alpha sample. Especially if there are not many alpha emitters present and they are not quenched by the sample itself. It can also be used to screen samples. In figure 6 one can see beta emissions on the right hand side of the spectrum and on middle and left the alpha peaks can be found.

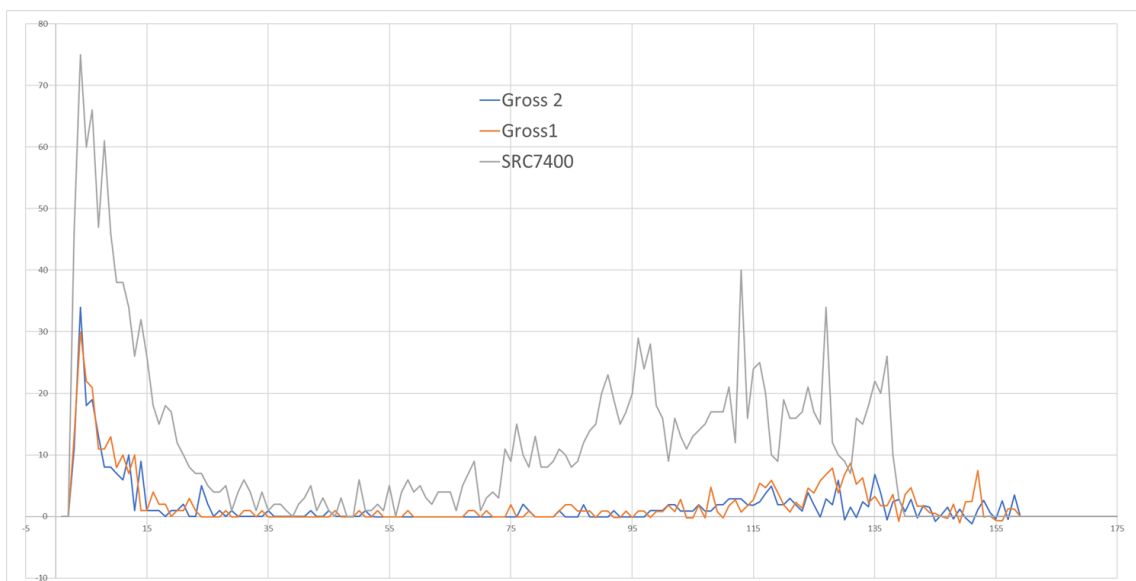


Figure 6: Gross alpha spectra of an aerosol filter and a swipe sample spiked with tracers (Gross 1 & 2) and the calibration source (SRC7400)

4.3 Sample matrices and pretreatment

4.3.1 Liquid matrices

Multiple different liquid matrices were used to test the capability of the separation method. These are listed below

- primary coolant; determination of baseline for tracer studies
- Primary coolant with tracers; determination of recoveries and linearity
- Primary coolant during layover; determination of effects due to changes in coolant chemistry
- Primary coolant with added boric acid; determination of boric acid interference
- Waste water before evaporation; determination of effects due to increased ionic strength

4.4 Validation of methods

The Eichrom method [84] discussed earlier was intended to be validated for measurements of U, Pu and Am/Cm from the primary coolant. The initial validation scheme is presented in table 2. Due to time restrictions, shortage of certain chemicals and other factors related to the measurement equipment the the full validation couldn't be performed within the scope of this work. Some of the validation experiments could be performed but a separate validation report will be produced.

4.4.1 Minimal detectable activity, MDA

The MDA function for a 95 % confidence level ($\alpha = \beta = 0.05, k = 1.645$) transforms into the form presented in equation 4. The background count rate varies with each PIPS detector. The effect of yield and background count rates is visualised in figure 7 where the MDA is counted for a 1 L sample. The observed background rates varied from 0 to about 0.01 counts/hour. The background rates will grow with time due to daughter nuclide deposition into the detector surface for this reason it is advisable to have multiple PIPS-detectors reserved for samples with very low activities.

$$MDA = \frac{2.71 + 3.29(\mu_B)^{1/2}(t_s)^{1/2}(1 + t_s/t_B)^{1/2}}{t_s * \epsilon * Y * S} \quad (4)$$

Where μ_B is the background count rate, t_s & t_B are count times for sample and background, ϵ is the efficiency of the counter, Y is yield and S is the sample amount. [69]

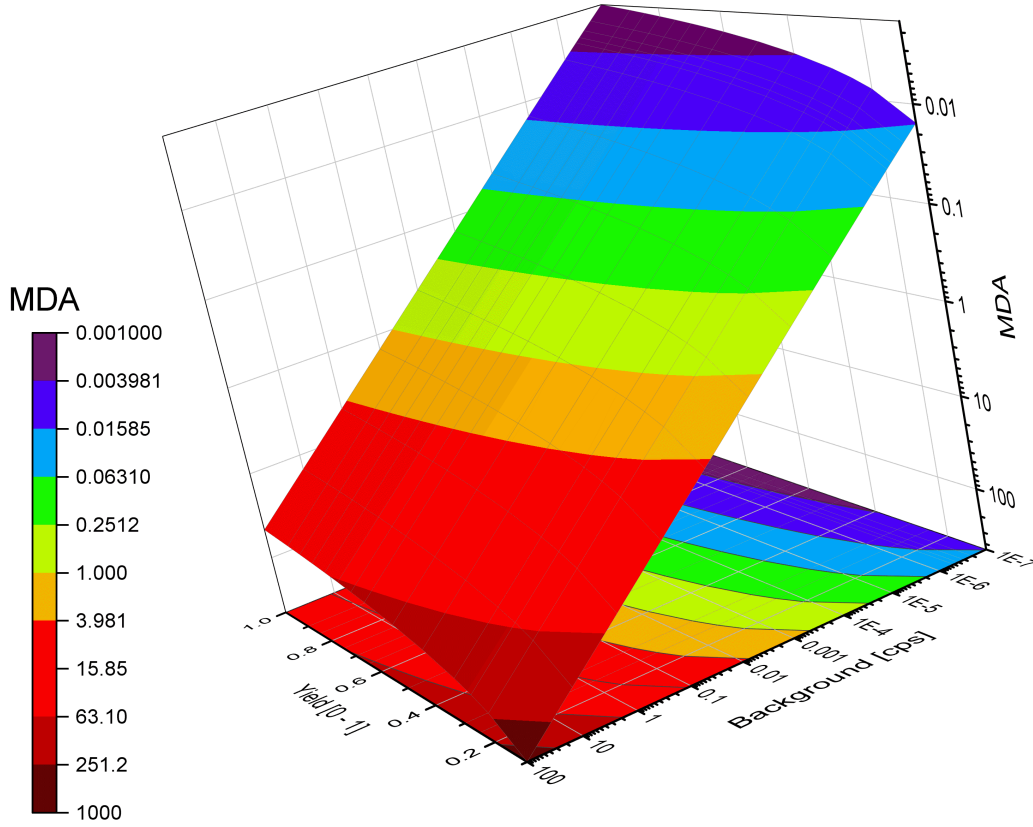


Figure 7: MDA in Bq/sample as a function of yield and detector background

Table 2: Validation scheme for primary coolant with the TEVA/TRU method.

| Analysis | Samples |
|------------------------------------|---------------------------------------------------------------------------------------------------------------------|
| Linearity U, Pu, Am | 0.005 Bq/l, 0.100 Bq/l, 5.0 Bq/l |
| Yield per nuclide 3 x 2 samples | Primary coolant during production Primary coolant during layover (high $[H_3BO_3]$) Intercalibration samples |
| Repeatability of measurements | Repeated measurements of same samples |
| Reproducibility of measurements | Replicate samples analysed Preferably by different individuals |
| MDA | Background- and yield measurements |

4.4.2 Effects of different matrices

During the experimental phase the Eichrom method presented earlier gave excellent results and recoveries from water samples. Effect of boric acid is under investigation, but preliminary testing shows also good results for separation. High boric acid concentrations might cause problems if boric acid recrystallises on surfaces thus blocking the flow of the liquids. Boric acid can be removed with formation of soluble $[BF_4]^-$ complex.

Usage of the method was tested on other sample matrices that were pretreated in a way so that the samples were destroyed and dissolved into dilute acid. Those sample matrices were: resin wastes, swipe samples and air filters. These matrices didn't seem to affect the efficiency of the separation if the pretreatment and dissolution of the filters was complete. If the sample matrix was not digested properly by the acid in the pretreatment phase, the solids present in the loading phase of the extraction obstructed the flow in the topmost resin cartridge so that the analyte had to be pushed thru the cartridge with help of a syringe plunger placed in the reservoir (syringe barrel). Thus it was possible to get the liquid flow thru the cartridge, but tracer yield was lower, also one has to take into account the possibility of analytes that are not digested in by the acid.

4.4.3 Ion exchange resin

Waste resins have been analysed at an external laboratory, those results are listed in table 9. Four samples were taken from larger sample batches. The samples, 1 mL each, were inserted into tared plastic test tubes, were weighed, dried and reweighed. The sample was measured with gamma spectrometry and then it was digested with help of nitric acid and microwawe digestion per internal lab procedure. The resulting liquid was evaporated to dryness and the resulting residue was dissolved into nitric acid and evaporated again. The residue was then dissolved into the loading solution (3 M HNO_3 / 1 M $AlNO_3$) and the sequential separation was performed on the samples. The results obtained were compared to the results from the external laboratory. The comparison is presented in section 5.4

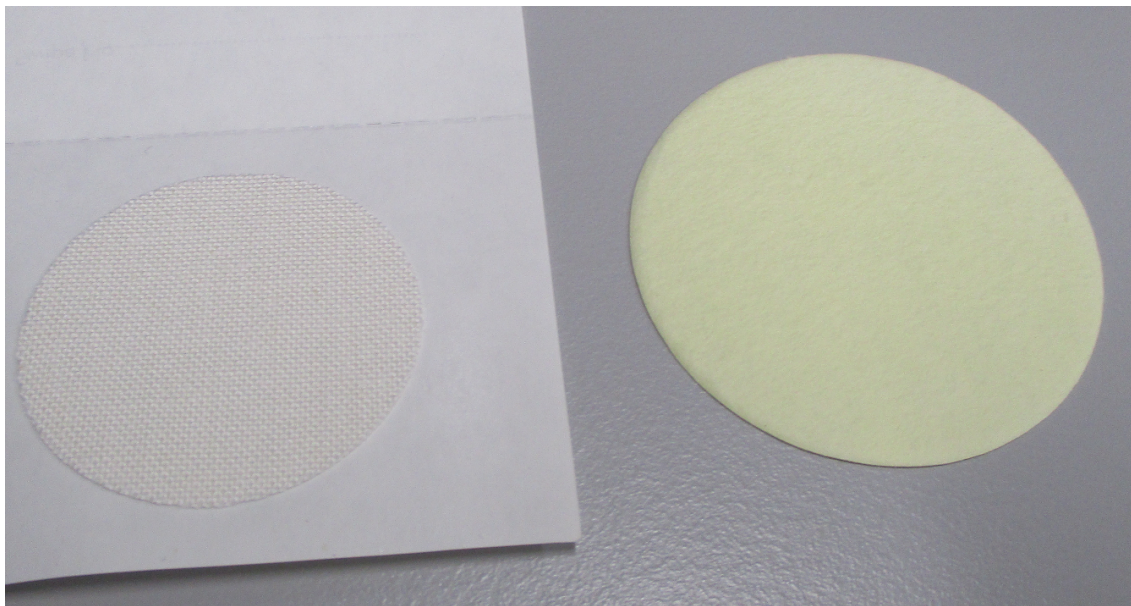


Figure 8: Swipe sample attached to the paper back and an aerosol filter

4.4.4 Surface swipes

Alpha activity was found from surfaces on parts of the upper reactor assembly that were removed earlier from the reactor. These parts called intermediate rods, or connecting rods, are being cut to reduce volume of highly radioactive waste. The upper parts of intermediate rods are not highly contaminated nor activated and these upper parts can be handled as normal contaminated metal waste. The lower parts on the other hand have been activated by the neutron flux of the reactor and are much more radioactive. [70] The intermediate rods are stored in a dry silo within the reactor building waiting for decommissioning of the plant. The dry silo will be decommissioned as a whole and the amount of space is limited. Thus freeing space in the dry silo is important when considering the extension of the operating period of the plant. [71]

The swipes were analysed first by the radiation protection organisation and a few samples that showed alpha-activity were selected for further study. They were first measured for gamma-emitting nuclides and then gross alpha and beta activity was determined with iSolo counter.

The swipe was then transferred into a beaker and tracers were added on top of the sample. The beaker was heated on low heat until the tracer solutions had dried, then the sample was ashed for 1 - 2 hours on high heat, until no further reduction in the sample could be observed. The ashing was done to reduce the mass of the

sample to a more suitable amount for the acid digestion and to destroy the glue that is used in the swipes to attach the swipe to the paper back. The swipe and an aerosol filter are presented in picture 8. The resulting ash was transferred to a Teflon beaker used in a microwave assisted digestion system. The beaker used for the ashing was washed with concentrated nitric acid and the liquid was transferred into the same beaker. The sample was digested in microwave assisted digestion system (MARS 5, CEM Corporation, USA) and the resulting liquid was again transferred into separate teflon beaker. The beaker was heated until the sample was dry.

The residue was dissolved into a small amount of concentrated nitric acid and was divided into two equal parts. One part was analysed with the Eichrom method (chapter 4.2.1) and the other part was analysed with the faster DGA-based gross alpha method presented earlier in this text (chapter 4.2.5)

4.4.5 Air filters

A rapid method for digestion of different aerosol filters is documented by US Environmental Protection Agency, in this method any filter regardless of composition can be digested in less than 2.5 hours, the end product is a dry residue from a HNO_3 liquid. This residue can then be dissolved into dilute acid, for example 1 M nitric acid or the loading solution for either the gross alpha method or the nuclide specific method. [72]

Aerosol samples have been analysed with a similar setup that was tested in this work at Waste Isolation Pilot Plant (WIPP). WIPP handles actinide waste generated mainly from defence related activities that are above the limit for low-level waste in the US. WIPP is located near Carlsbad, NM and operates an environmental monitoring program that collects aerosol filters from the plant (intake and exhaust) and in the vicinity of the plant. Water, soil and other samples are also analyzed with americium and plutonium being the main transuranium elements analysed. [73]

Usually one half of the exhaust air filter (47 mm membrane Versapor filter) is digested with a mixture of concentrated nitric-, hydrochloric- and hydrofluoric acids with a microwave digestion system ($T_{max} = \text{ }^\circ\text{C}$ and hold time 10 min). After microwave digesting the acids are evaporated and complete digestion of the residue is achieved by HClO_4 . The perchloric acid is used due to diesel particulates present in the samples that are not digested in the previous phase and to remove any fluorine from the sample. [73]

Aerosol filters (20 x 25 cm, A/ETM glass fiber filters) are first ashed in a furnace (500 °C) for 6 hours and then tracers are added. The ash is dissolved using HNO₃ and HF and then the liquid is evaporated to remove fluoride ions. Additional HNO₃ is used to rinse the walls of the beaker to ensure complete removal of fluoride. The sample is again evaporated and the residue dissolved in mild acid. [73]

Alpha activity has been also analysed from plant air filter from Olkiluoto. The yields from the air filter samples were compared between wet ashed, acid leached and water leached methods. The recoveries reported were over 50 % for most of the samples. A MDA of 0.01 Bq of ²⁴¹Am is reported to achieved on a collection time of 2 days and much lower on the samples during normal operations when the collection time is about 4 weeks. [74]

5 Results and discussion

5.1 Measurements performed

Following measurements and samples were made and analysed during the course of this work. The samples can be divided to a few categories. 1) Water samples used in validation analysis, 2) various other matrices tested for matrix and pretreatment effects, 3) intercalibration samples and 4) Unknown samples to be analyzed.

- Primary circuit water (various H_3BO_3 and tracer concentrations as part of the validation scheme)
- Gross alpha (DGA)
- Thorium free tracer for high tracer activity samples
- Waste water to be evaporated
- Waste resin
- Fuel pool water, intercalibration sample
- Lichen and sediment samples, intercalibration
- DGA-separation series to optimize conditions
- Aerosol filters, pretreatment and yield determination for spiked samples,
- Surface swipe samples, pretreatment and yield determination for spiked samples, assessment of nuclide composition and variation of sample activity with different measurement equipment

5.2 Coolant water samples

The samples from coolant constituted from both primary circuit water and fuel pool water. The results from the primary coolant samples is presented in table 3 and in figures 9 and 10.

The first test, without any tracers, only using primary coolant seemed to give positive results, but the activities were so low that no actual value could be determined. There were peaks in the spectrum that rose above the surrounding background, but

the levels seemed to be too low to give a valid result, increasing the measurement time or sample amount might reveal the peaks better or dismiss them as noise. These activities were found in U and Am/Cm fractions, no activity was detected in the Pu fraction. Very little actinides should be present during normal power production.

The initial test with tracers (^{242}Pu and ^{243}Am) gave very positive results with recoveries over 95 % for Pu and Am. For the first samples uranium recovery had to be estimated from an U-234/235/238 solution because no tracer solution (U-232) was available at the time of separation.

Boric acid concentration should not be a problem if the phosphate precipitation step is carried out, the elevated pH of the solution should keep boric acid in the tetraborate -ion $[B(OH)_4]^-$

When remeasuring older samples the ingrowth of daughter nuclides could be observed as increased events, usually outside the regions of interest used. This most obvious in the samples containing high activities that were analysed a few months after the initial separation. This means that the most accurate results are achieved before any significant ingrowth happens.

Table 3: Yield of nuclides from primary coolant, with varying activity in sample

| concentration sample | | 0,005 Bq/L | 0,100 Bq/L | 0,5 Bq/L | 5,0 Bq/L |
|-------------------------|-----|------------|------------|----------|----------|
| Primary coolant | Pu: | 89 % | 102 % | 72 % | 68 % |
| | Am: | 91 % | 100 % | 84 % | 92 % |
| | U: | 76 % | - % | 93 % | 83 % |

5.2.1 Waste water before evaporation

A water sample of 1 liter containing about 3 grams of boric acid and an additional 5 grams of other residual matrix constituents was split into two fractions and processed with the method described in section 4.2.1 and the results are tabulated below in table 4.

5.2.2 Fuel pool water

The fuel pool sample was received from an intercomparison test [75] where multiple Nordic laboratories participated. The results of the intercomparison study are pre-

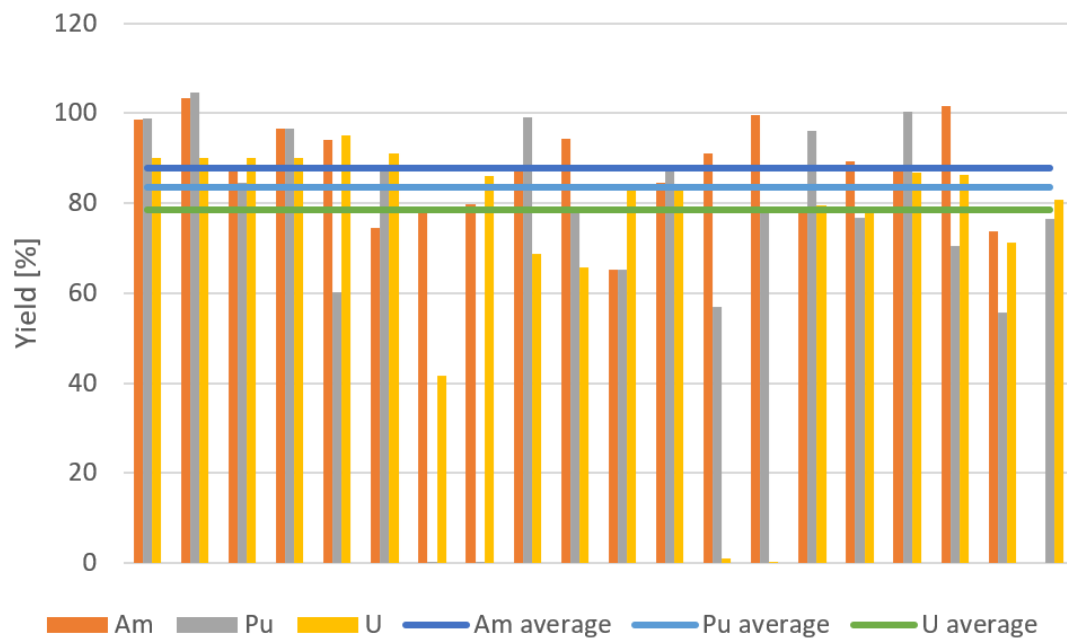


Figure 9: Tracer yield from primary coolant

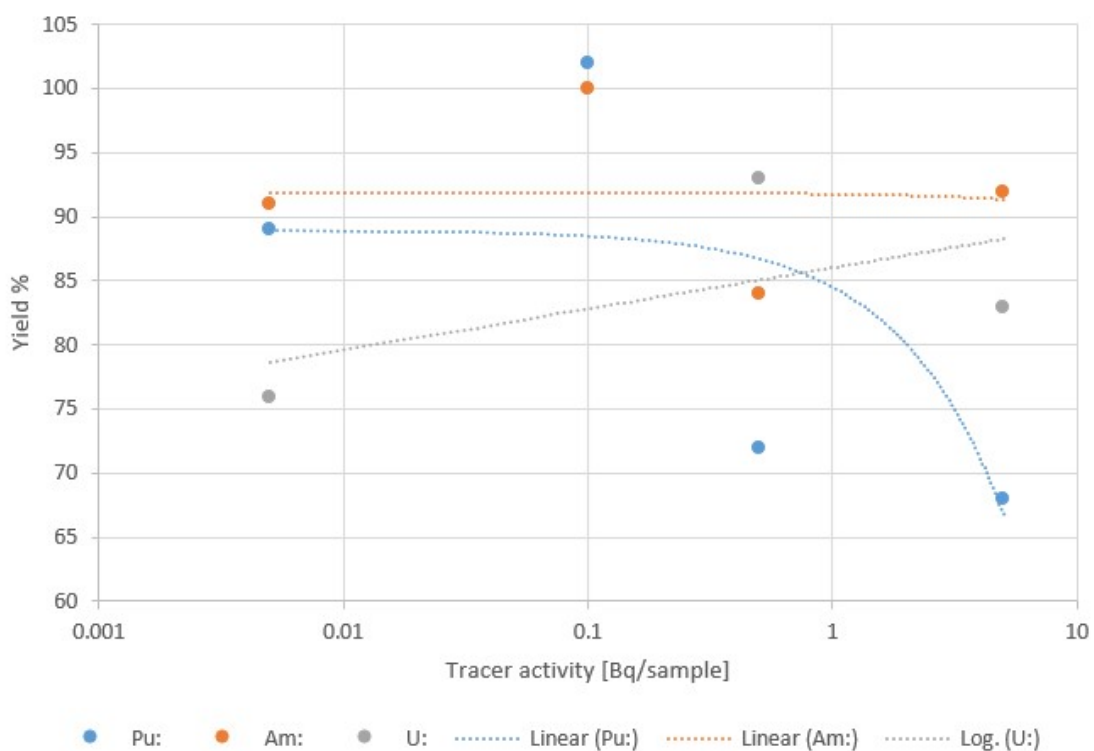


Figure 10: Tracer yield, with function of tracer activity

Table 4: Results of waste water samples

| Nuclide | Bq/L | 1σ | MDA Bq/L | average recovery |
|---------|----------|-----------|----------|------------------|
| Pu-238 | 2,49E-02 | 5,14 | 6,20E-04 | - |
| Pu-239 | 1,50E-02 | 6,51 | 4,41E-04 | - |
| Pu242 | 3,49E-01 | 1,35 | 3,58E-04 | 103,35 |
| Am-241 | 2,71E-02 | 5,69 | 8,52E-04 | - |
| Cm-242 | 3,02E-02 | 5,40 | 2,07E-04 | - |
| Am243 | 2,70E-01 | 1,95 | 8,07E-04 | 62,80 |
| Cm-244 | 1,34E-02 | 7,77 | 2,05E-04 | - |
| U232 | 9,50E-01 | 1,35 | 2,14E-04 | 80,98 |
| U-234 | 3,03E-03 | 16,09 | 2,14E-04 | - |
| U-235 | 4,53E-04 | 47,38 | 2,64E-04 | - |
| U-238 | 2,03E-03 | 19,54 | 2,13E-04 | - |

sented in table 5. Uranium isotopes were also determined, but no uranium tracer was available at the time of the separation, thus no analytical results were achieved, only the activity ratio of uranium isotope-activities could be determined (1.082:0.258:1) for ^{234}U : ^{235}U : ^{238}U when normed to the activity of uranium-238. The pool is known to contain used fuel. The results of the inter-comparison test are also presented in table 5 and in the figure 11 where the all the results of the intercalibration exercise are plotted.

Table 5: Results of fuel pool water intercalibration sample

| Nuclide | mBq/L | 1σ | NKS-436 | 1σ | average recovery |
|------------|--------|-----------|---------|-----------|------------------|
| Am-241 | 5,15 | 0,45 | 4.71 | 0.4 | - |
| Am-243 | 99,83 | 2,1 | - | - | 92 % |
| Cm-242 | <1,43 | 0,7 | - | - | - |
| Cm-244/243 | 2,83 | 0,33 | 2.27 | 0.44 | - |
| Pu-238 | 19,69 | 0,91 | 19.4 | 2.0 | - |
| Pu-239/240 | 0,68 | 0,17 | 1.10 | 0.39 | - |
| Pu-242 | 108,55 | 1,95 | - | - | 90 % |

5.3 DGA based methods

Different recipes were tried to achieve separation of different radionuclides from interfering daughters and other radionuclides. The principal idea was to load the

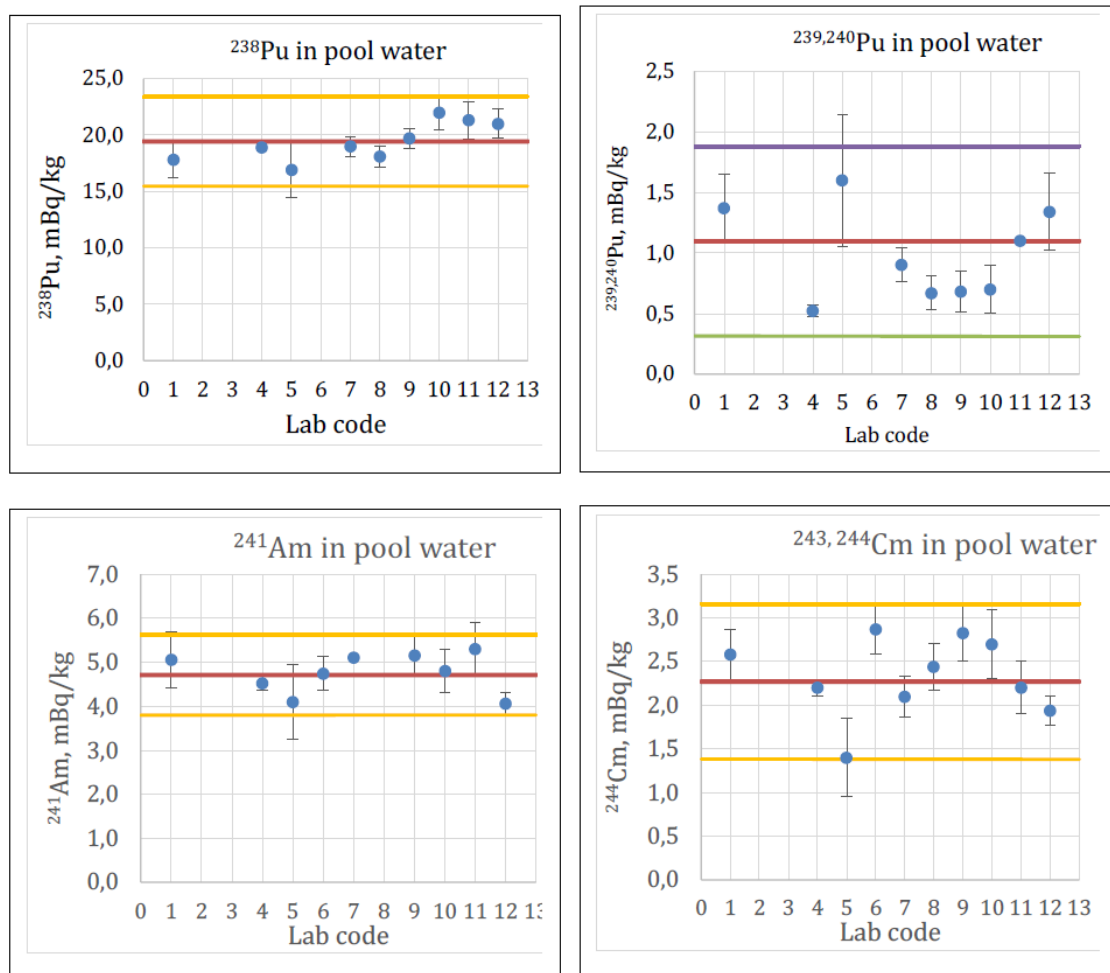


Figure 11: Results of fuel pool water intercalibration between laboratories participating [75]

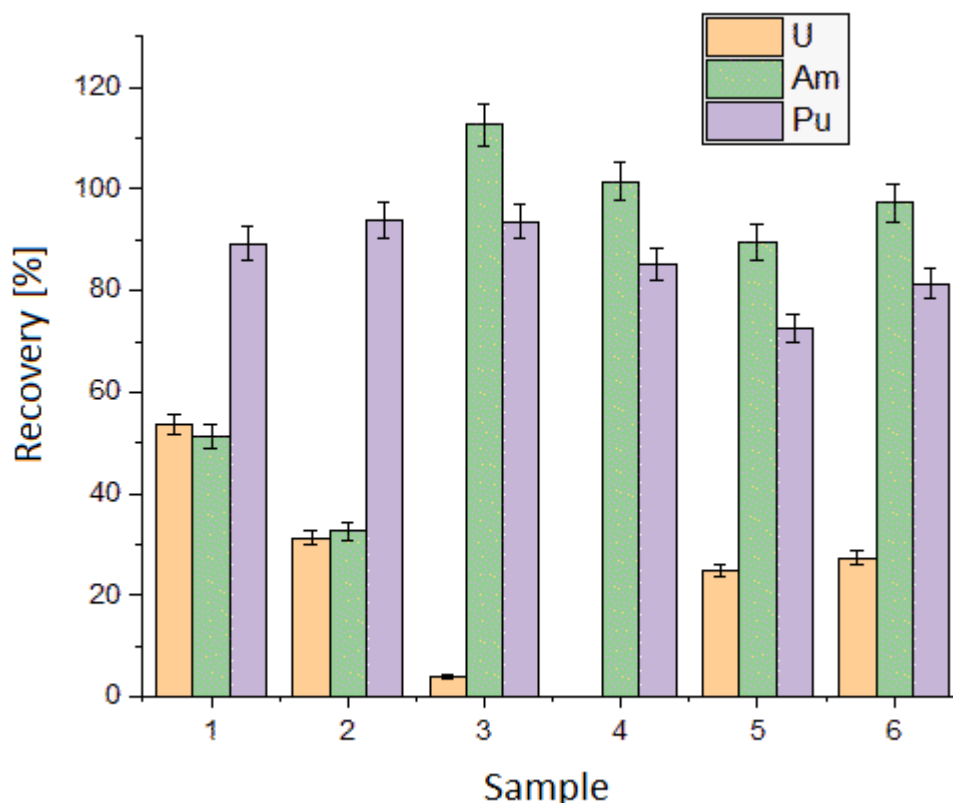


Figure 12: Yields of nuclides in different DGA samples, samples 1-6 on axle A and on axis U is the recovery in %

columns with a loading solution (10 mL 3 M HNO_3 /0.1 M NaNO_2) containing the appropriate tracers, then rinse the column with 10 mL of 3 M HNO_3 . After this U, (Th), Am and Pu could be eluted from the column using nitric- and hydrochloric acids and oxidation state changes. Thorium was removed with 25 mL of 0.5 M HNO_3 + 0.05 M oxalic acid + 0.01 M Fe(II)

The different schemes and results are presented in table 6 and in appendix 3. The results are presented in figure 12 As it can be seen from the results the recoveries for Pu and Am stay about the same in the samples 3-6 and uranium recoveries are smaller in all fractions. This has to do with the high affinity of DGA to trivalent actinides. Uranium on the other hand is present as tetra- or hexavalent and might need an oxidation state change to better control the recovery of U, both to minimize the bypass of uranium ions into unwanted fractions and ensuring the elution of U in the proper stage.

Table 6: The different DGA schemes

| Sample | U | U yield | Th removal |
|--------|---------------------------------------------------------|-------------------|-----------------------------|
| 1 | 20 mL 0.1 M HNO ₃ | 53,64 +/- 3.75 % | no |
| 2 | 20 mL 0.1 M HNO ₃ | 31,28 +/- 4.51 % | no |
| 3 | 20 mL 0.5 M HNO ₃ + 0.03 M NaNO ₂ | 3,82 +/- 10.37 % | no |
| 4 | 20 mL 0.5 M HNO ₃ + 0.03 M NaNO ₂ | >MDA % | no |
| 5 | 20 mL 0.5 M HNO ₃ | 24,68 +/- 4.70 % | yes |
| 6 | Reduction (10 ml 4 M HCl + 0,05 M Fe(II)) | 27,37 +/- 4.63 % | yes |
| Sample | Am | Am Yield | Pu |
| 1 | 20 mL 0.1 M HCl + 0.03 M NaNO ₂ | 51,33 +/- 4.68 % | 20 mL 0,1 M HCl+0.01 M TiCl |
| 2 | 20 mL 0.1 M HCl + 0.03 M NaNO ₂ | 32,58 +/- 5.48 % | 20 mL 0,1 M HCl+0.01 M TiCl |
| 3 | 20 mL 0.5 M HCl + 0.01 M NaNO ₂ | 112,64 +/- 3.65 % | 20 mL 0,5 M HCl+0.02 M TiCl |
| 4 | 20 mL 0.5 M HCl + 0.01 M NaNO ₂ | 101,43 +/- 3.72 % | 20 mL 0,5 M HCl+0.02 M TiCl |
| 5 | 20 mL 0.5 M HCl + 0.01 M NaNO ₂ | 89,53 +/- 3.87 % | 20 mL 0,5 M HCl+0.01 M TiCl |
| 6 | 20 mL 0.5 M HCl + 0.01 M NaNO ₂ | 97,30 +/- 3.76 % | 20 mL 0,5 M HCl+0.01 M TiCl |
| | | | Pu yield |
| | | | 89,25 +/- 3.72 % |
| | | | 93,80 +/- 3.67 % |
| | | | 93,63 +/- 3.61 % |
| | | | 85,11 +/- 3.71 % |
| | | | 72,67 +/- 3.89 % |
| | | | 81,44 +/- 3.76 % |

5.4 Environmental and waste samples

An IAEA reference material (IAEA-384) was analysed with a TEVA/DGA scheme and the results are presented in table 7 and in figure 13. The samples were digested in MARS 5 with nitric acid with in 200 °C for 15 minutes. The samples were then separated with a stacked TEVA/DGA column and Am, Pu and U fractions were separated. The uranium fraction was lost due to a problem with the reduction of U(VI) to U(IV) with TiCl_3 , probably due TiCl_3 expiration. A sample of lichen was also analysed and the recoveries were also >90 % and the uranium fraction was also lost due to the same reason as in the sediment sample. There was an intention to separate this reference sample also with the TEVA/TRU method and compare the results, but due to time constraints and unavailability of chemicals this couldn't be performed.

Waste resins and evaporation waste samples were analysed for both their gamma and alpha-activities. The same material has been previously analysed at an external laboratory, both gamma and alpha-activities from both samples are tabulated into tables 8 and 9. These samples were analysed with the TEVA/TRU method.

A larger amount of the resin used to clean the primary circuit was also analysed with the nuclide specific method. The samples were first weighed, dried and reweighed, then the samples were digested, in parts of 0.5 g, with a microwave assisted digestion system per lab protocol. The digested samples were then merged back together and the resulting liquid was evaporated. A small amount of residue was left that could not be digested, even with additional microwave digestion in HCl/HNO_3 nor with addition of HF to the sample. The sample was then again evaporated and dissolved into the loading solution and the sample was separated with the method described in the earlier sections.

Table 7: IAEA-384 measured activity, yield and reference values for activity

| Nuclide | Average yield | mBq/g | Certified value IAEA-384 |
|---------|---------------|----------------|--------------------------|
| AM-241 | 98 % | 9.9 ± 0.8 | 9.3 ± 1 |
| PU-238 | 103 % | 38.1 ± 1.6 | 32.7 ± 0.6 |
| PU-239 | | 98.2 ± 2.6 | 108 ± 13 |

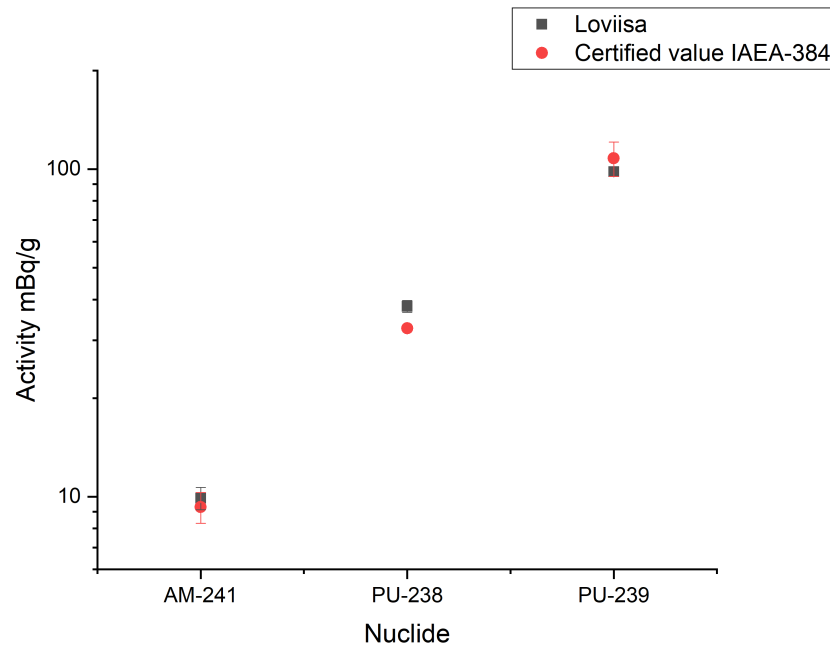


Figure 13: IAEA-384 activity, measured and reference values

5.5 Surface swipe samples

Swipe samples described in part 4.4.4 were analyzed with multiple different techniques. Radiation protection measured the activity with a portable device and estimated an alpha activity of 4-5 Bq.

Measurement with iSolo yielded an activity of 5,68 Bq. The spectrum is presented in figure 14. In the picture only the continuous alpha/beta spectrum can be seen with a sharp decline seen at maximum alpha energy. Gamma-activities measured were ^{60}Co (399 Bq), ^{94}Nb (10,7 Bq) and ^{241}Am (4,43 Bq). Gross alpha with DGA showed an activity of around 4,7 Bq of alpha activity when taking into account the amount of tracer activity added. The spectrum produced by the DGA-method is presented in figure 15 as Gross alpha.

The nuclide specific method yielded an alpha activity of 4,92 Bq over the different fractions. There was significant interference from the Am-241 peak on the tracer peak (Am-243) and if assuming a recovery of 100 % then the gross alpha activity is 5,4 Bq. The combined spectras of these three fractions is also presented in figure 15. The alpha activity is divided between three major alpha emitters; Am-241, Pu-238 and Pu-239/240. Their respective activities are presented in table 11. As it can be seen from the figure and the table 5.5 most of the interesting nuclides have

Table 8: Gamma emitters present in waste resin. Two different resin samples were analysed with two subsamples from both. Activities in Bq/m³

| | | | | | | | |
|----------------|----------------------|-------|----------------------|------|----------------------|-------|-------|
| sample | Mn-54 | % | Co-60 | % | Ag-108m | % | |
| 1 ₁ | 4,79*10 ⁴ | 31,03 | 2,79*10 ⁶ | 3,73 | 8,17*10 ³ | 30,85 | |
| 1 ₂ | 7,85*10 ⁴ | 32,93 | 5,30*10 ⁶ | 4,18 | 1,43*10 ⁴ | 16,92 | |
| 2 ₁ | - | - | 3,22*10 ⁶ | 3,73 | 1,94*10 ⁴ | 12,46 | |
| 2 ₂ | - | - | 3,30*10 ⁶ | 4,19 | 2,07*10 ⁴ | 13,5 | |
| sample | Sb-125 | % | Cs-134 | % | Cs-137 | % | Co/Cs |
| 1 ₁ | 4,75*10 ⁴ | 53,16 | 1,21*10 ⁶ | 2,41 | 1,44*10 ⁷ | 3,94 | 19 % |
| 1 ₂ | - | - | 1,23*10 ⁶ | 2,7 | 1,44*10 ⁷ | 4,57 | 37 % |
| 2 ₁ | 6,86*10 ⁴ | 18,13 | 5,73*10 ⁵ | 2,68 | 1,14*10 ⁷ | 3,94 | 28 % |
| 2 ₂ | 4,66*10 ⁴ | 23,59 | 5,69*10 ⁵ | 3,18 | 1,19*10 ⁷ | 4,57 | 28 % |

Table 9: Alpha emitters present in waste resin. Two different resin samples were analysed at an external laboratory and Loviisa. Activities in mBq/ml

| | | | | | | |
|----------------|------------|------|--------|------|--------|------|
| sample | 239,240 Pu | | 238Pu | | Am241 | |
| External lab. | | +- | | +- | | +- |
| 1 | 75,10 | 4,43 | 110,00 | 6,44 | 110,00 | 6,44 |
| 2 | 52,30 | 7,68 | 64,80 | 9,34 | 64,80 | 9,34 |
| sample | 239,240 Pu | | 238Pu | | Am241 | |
| Loviisa | | +- | | +- | | +- |
| 1 ₁ | 117 | 3,51 | 152 | 3,4 | 426 | 7,39 |
| 1 ₂ | 104 | 2,8 | 132 | 2,72 | 192 | 7,76 |
| 2 ₁ | 113 | 2,8 | 199 | 2,68 | 311 | 1,03 |
| 2 ₂ | 115 | 2,78 | 175 | 2,66 | 370 | 7,37 |

overlapping energies and they cannot be separated from gross alpha spectra. The alpha energies are taken from the *Database WWW Table of Radioactive Isotopes* and the Apex-Alpha software database [86], [76]

5.6 Remarks about the Eichrom method and vacuum box system

Within the scope of this work a method of adjusting the flow rate while using the VBS was employed. A stopwatch and reservoir volume change were used to

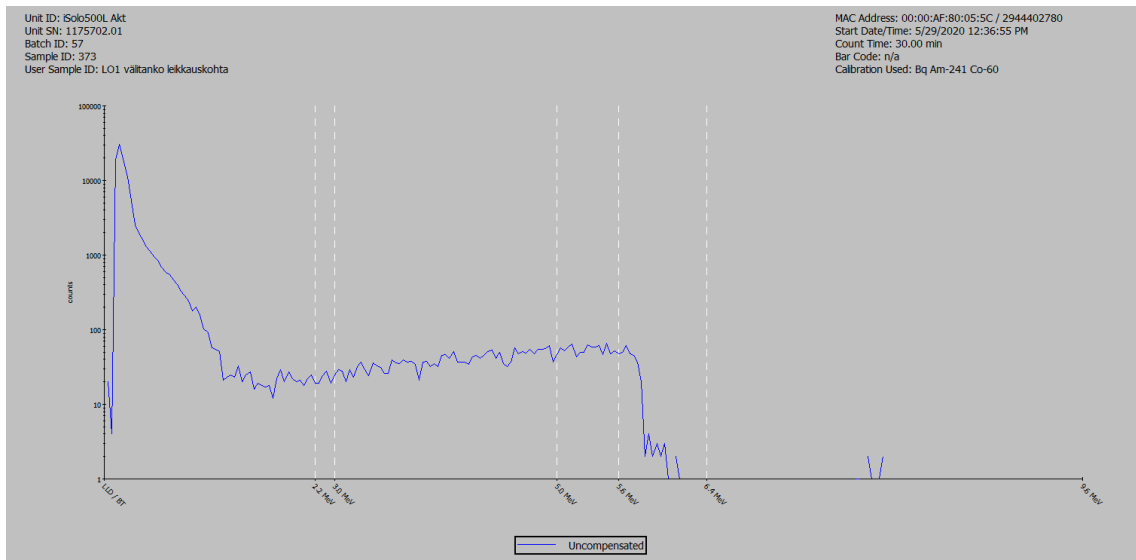


Figure 14: Spectrum of the surface swipe measured with iSolo

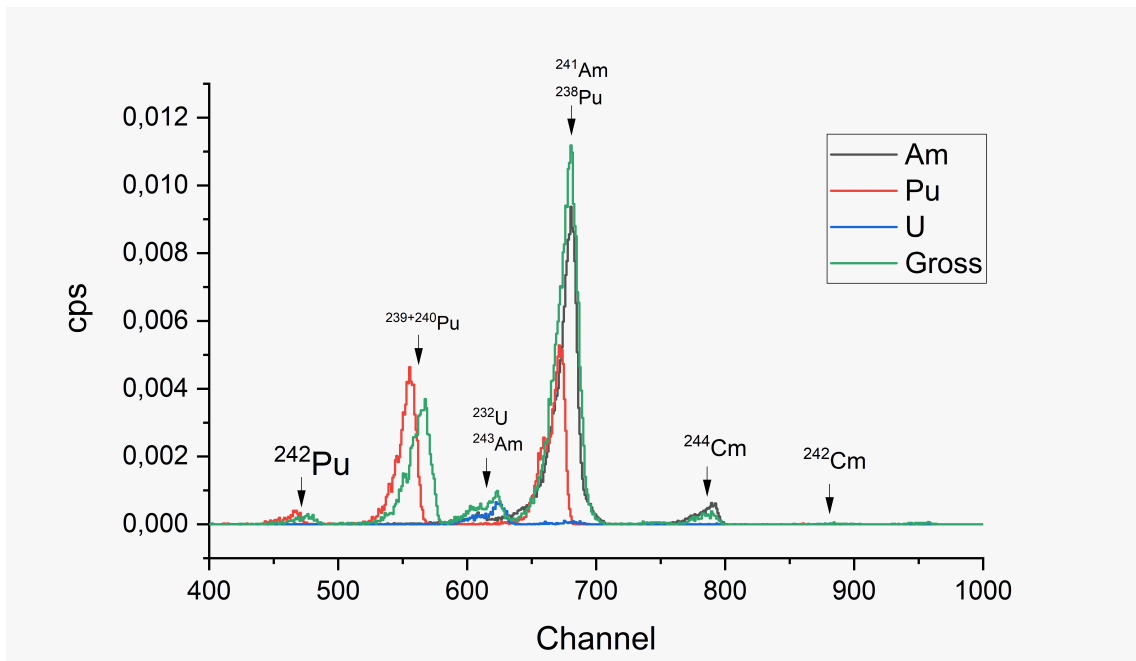


Figure 15: Alphaspectra of the surface swipes with both the gross alpha and nuclide specific methods

determine the flow rate. The flow rate (0.5 - 5 ml/min) was adjusted so that initially the fastest column achieved the desired speed and the pressure was adjusted if the other reservoirs were emptying very slowly. Syringe valves can be also to separate the columns from the vacuum after the fluids have passed thru. This enhances the flow rate of the remaining columns due to the vacuum not purging thru the empty

Table 10: Most intense alpha-energies of the nuclides under investigation

| Energy [keV] | Intensity [%] | Nuclide |
|--------------|---------------|-------------------|
| 4198 | 79 | ²³⁸ U |
| 4398 | 55 | ²³⁵ U |
| 4775 | 71 | ²³⁴ U |
| 4901 | 78 | ²⁴² Pu |
| 5157 | 73 | ²³⁹ Pu |
| 5168 | 73 | ²⁴⁰ Pu |
| 5275 | 87 | ²⁴³ Am |
| 5320 | 68 | ²³² U |
| 5486 | 85 | ²⁴¹ Am |
| 5499 | 71 | ²³⁸ Pu |
| 5804 | 76 | ²⁴⁴ Cm |
| 6113 | 74 | ²⁴² Cm |

Table 11: Alpha activities of swipe sample analysed with nuclide specific method

| Nuclide | Energy [MeV] | Peak area | Activity [Bq] | uncertainty [%] | Recovery |
|------------|--------------|-----------|---------------|-----------------|----------|
| Am-241 | 5,462 | 13524 | 2,2E0 | 4,78 | |
| Am-243 | 5,252 | 475 | 7,75E-2 | 4,70 | 122,6 |
| Cm-242 | 6,083 | 16 | 2,9E-3 | 25,74 | |
| Cm-244 | 5,775 | 966 | 1,58E-1 | 5,69 | |
| Pu-238 | 5,476 | 6527 | 1,32E0 | 5,04 | |
| Pu-239/240 | 5,139 | 5587 | 1,13E0 | 5,07 | |
| Pu-242 | 4,875 | 420 | 8,43E-2 | 4,89 | 99,18 |
| U-232 | 5,284 | 894 | 2,30E-1 | 3,49 | 77,74 |
| Total | | 28409 | 5,20E+00 | | |

column. In case of only a few columns the pressure couldn't be adjusted from the pump, it was regulated by opening the pressure relief valve seen in picture 5. A slight turn of the pressure valve achieved the desired effect, it was noted that regulating the pressure difference was more difficult with this way, due to the valve and the usually small amount of used columns. When performing the micro coprecipitation a much higher pressure could be used. This greatly enhanced the speed of the deposition. High pressure also dried the counting samples faster and made their application onto the sample holder disks a lot easier.

Precipitation of calcium phosphate can be enhanced and sped up with the use of

a cold water bath (a bucket). After precipitating for a while, decant main part of the liquid and centrifuge the remainder, or use larger centrifuge tubes, if available to centrifuge the whole volume.

Syringe plungers should be available if the cartridges get clogged and increasing the vacuum doesn't help unclogging them, then one can use the plunger to first apply pressure and then suck air thru the cartridge, this might open the cartridge enough so that the separation can be finished. If external pressure is applied the flowrate should be kept at minimum to reduce the creation of by-pass channels into to the resin cartridge.

5.7 Summary

The method presented for water matrices in this work will fulfill the demands for actinide analysis from primary coolant. If a need to assess actinide levels during normal operations without any indication of a fuel leak a preconcentration step is probably necessary. This can be performed by concentrating the liquid sample by evaporation, which is slow and unnecessary large amounts radioactive coolant is needed. Another possibility is to use ion exchange resins or extraction chromatography. For example the concentration can be easily performed with the actinide resin or TRU resins from a larger volume water sample that has been acidified to about 1M HNO_3 . Tetra- and hexavalent actinides will retain in even lower concentrations of HNO_3 , even from 50 mM solutions [24]

Most of the tested matrices could be analysed with ease with the Eichrom method and no significant problems could be identified during this work. The method described and tested is fast and reliant and can be used with little need of preparations if the chemicals needed for the separation are readily available in the laboratory. Certain chemicals are in short supply at this moment due to the COVID-19 pandemic and some replacement chemicals were tested, mainly for the oxidation state changes. Also some of the equipment meant for single use could be reused after throughout washing with water, soap and an acid bath. Despite this the parts used with the low activity samples were all brand new to minimize the amount of cross contamination. The lower yield of the uranium fraction compared to the Am and Pu yields is most probably caused by the expired chemical (TiCl_3) used to reduce uranium. This caused the uranium not already present as tetravalent in the solution to stay as hexavalent, which doesn't coprecipitate with the NdF_3 . This caused only the residual U(IV) to precipitate and the main part of the uranium to stay in the

solution which was then passed to the wastes. An solution to this would be to gather the load solutions to separate fractions, this in turn adds steps to the procedure.

The biggest problems related to the method can be associated with the always tedious pretreatment and concentration steps in which the complete destruction needs to be ensured to ascertain that all the analytes are in the liquid phase and the solids do not block or hinder the eluation steps.

The DGA methods tested showed promising results, especially the gross alpha method due to its speed. There was little difference between the TEVA/TRU and DGA methods in analysis time if the full nuclide separation was performed. The problems presented in the works done with DGA without temperature control and the smaller yields compared to the TEVA/DGA method mean that the latter is more suitable for the use intended in this work. The DGA resin could be used more easily in an autosampler and -separator system where all the steps are computer controlled and little involvement is needed from the person performing the analysis.

The next steps to take would be to perform the remaining separations and measurements to validate the method for the primary coolant. After this other matrices can be validated more easily if needed.

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Manuals

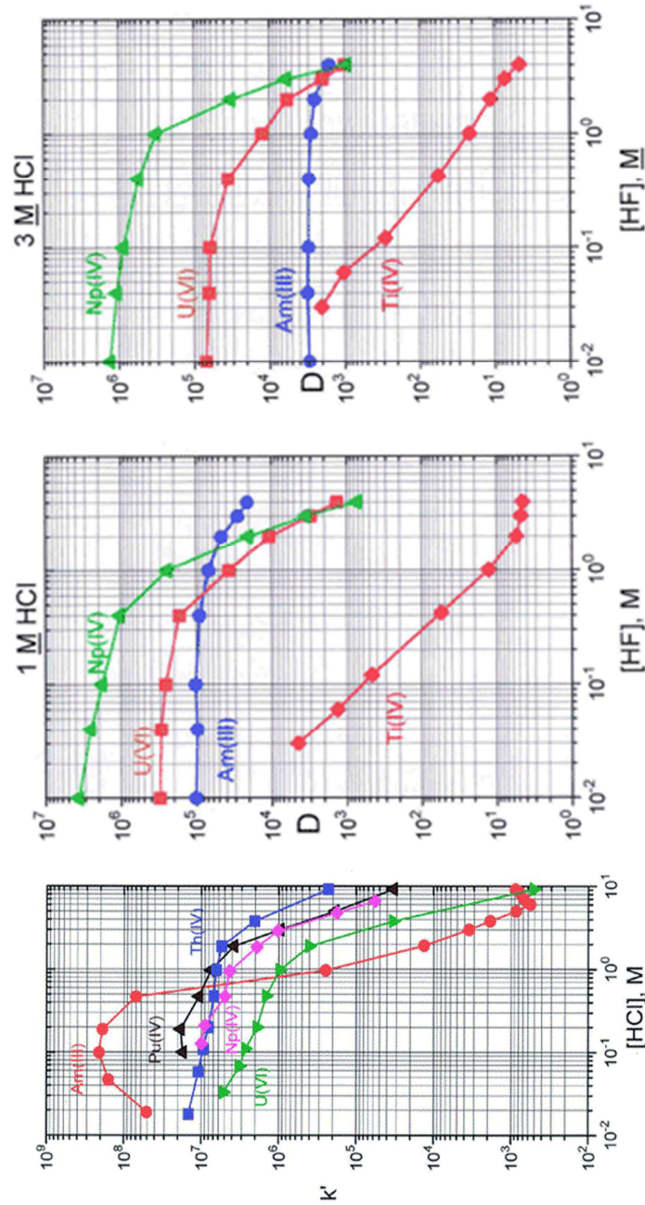
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Appendix 1.1. Effect of eluant properties on Actinide resin k'

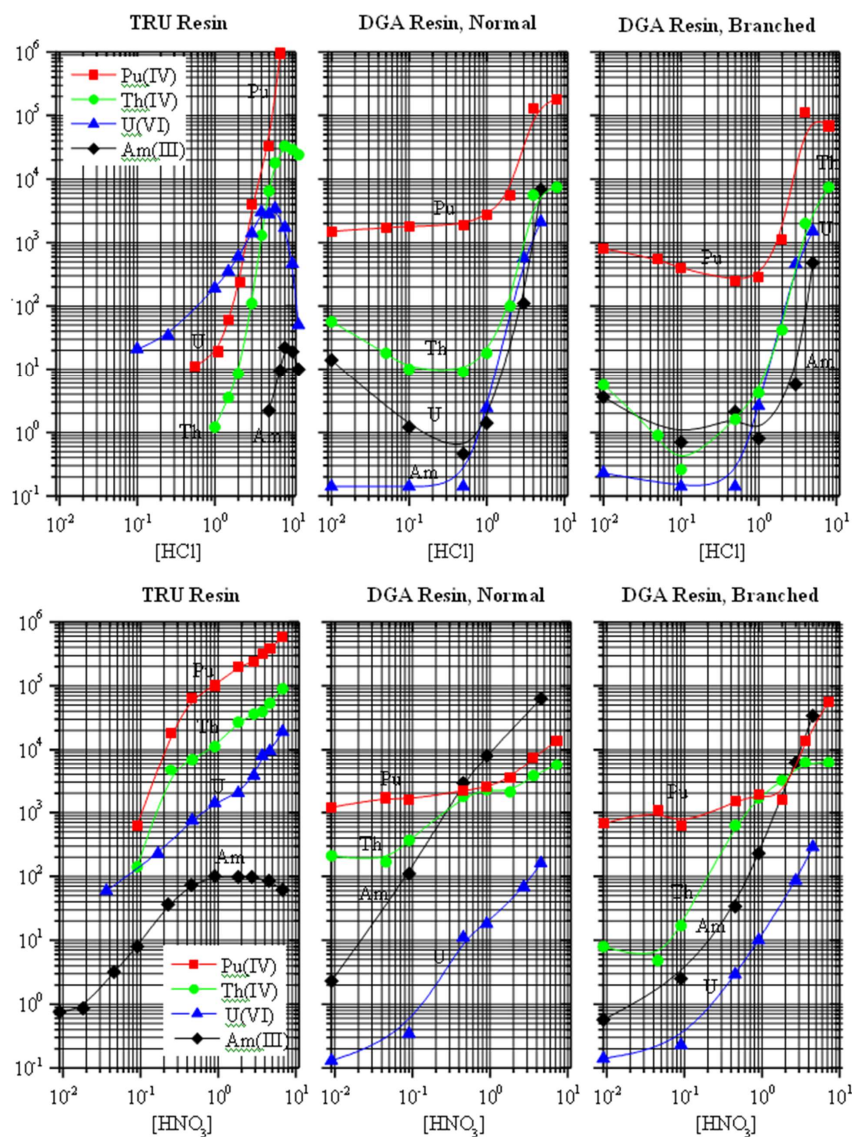


Effects of HF concentration change in 1 M HCl and 3 M HCl on k' in Actinide resin

Effects of HCl concentration on k' in Actinide resin

Data from [20], [83]

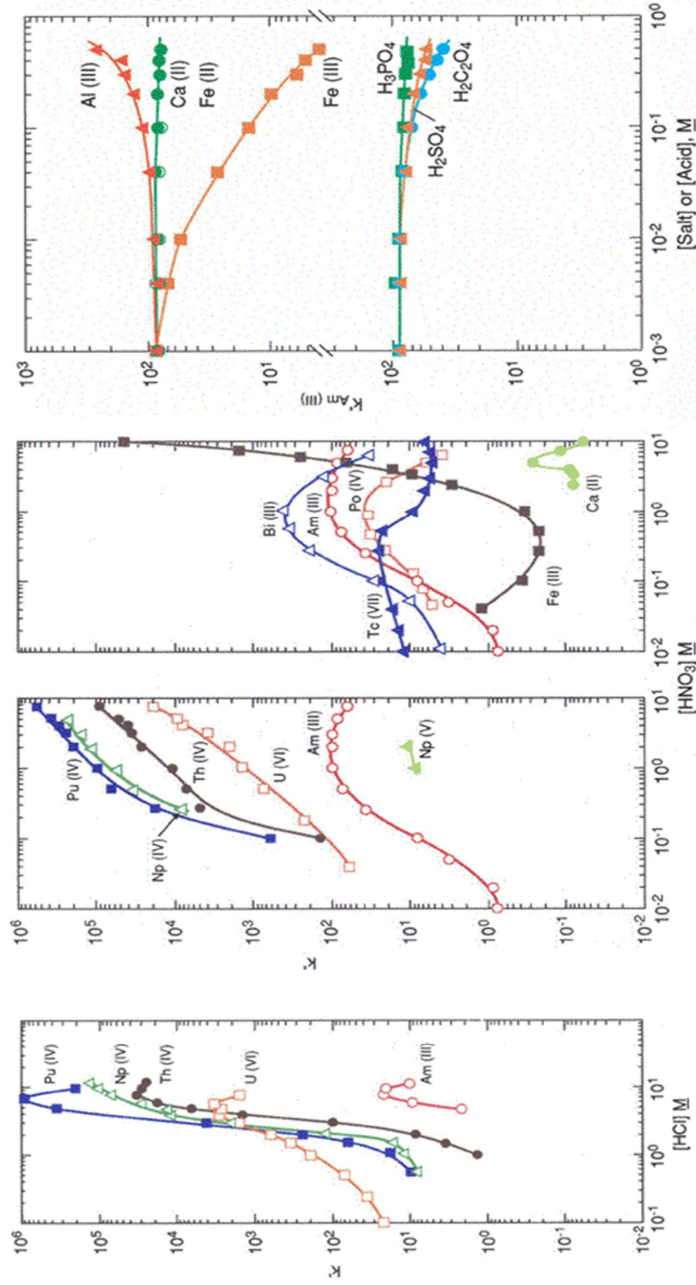
Appendix 1.2. Effect of eluant properties on DGA and TRU k'



Change in k' in with varying HCl and HNO₃ concentrations for various species in DGA and TRU

Data from [19], [78], [82]

Appendix 1.3. Effect of eluant properties on TRU k'

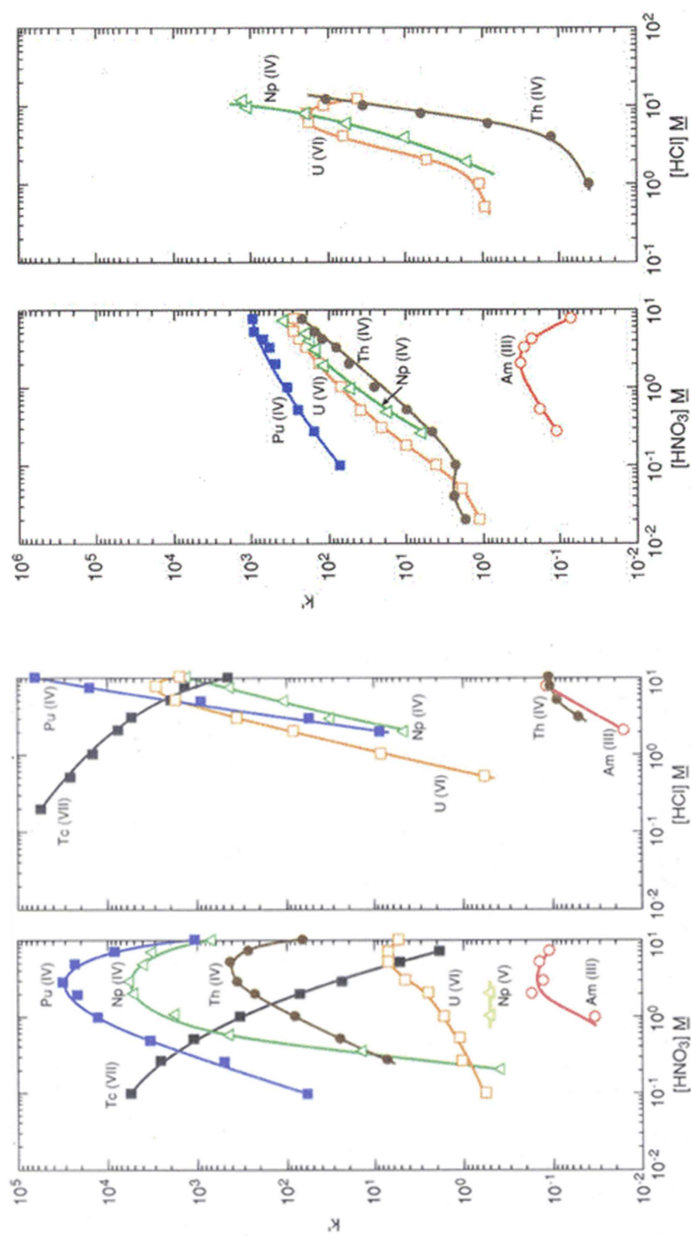


Effect on k' from interfering ions on Am(III) in 2M HNO_3 in TRU

Effects of HCl and HNO_3 concentration on k' for different ions in TRU

Data from [82], [24]

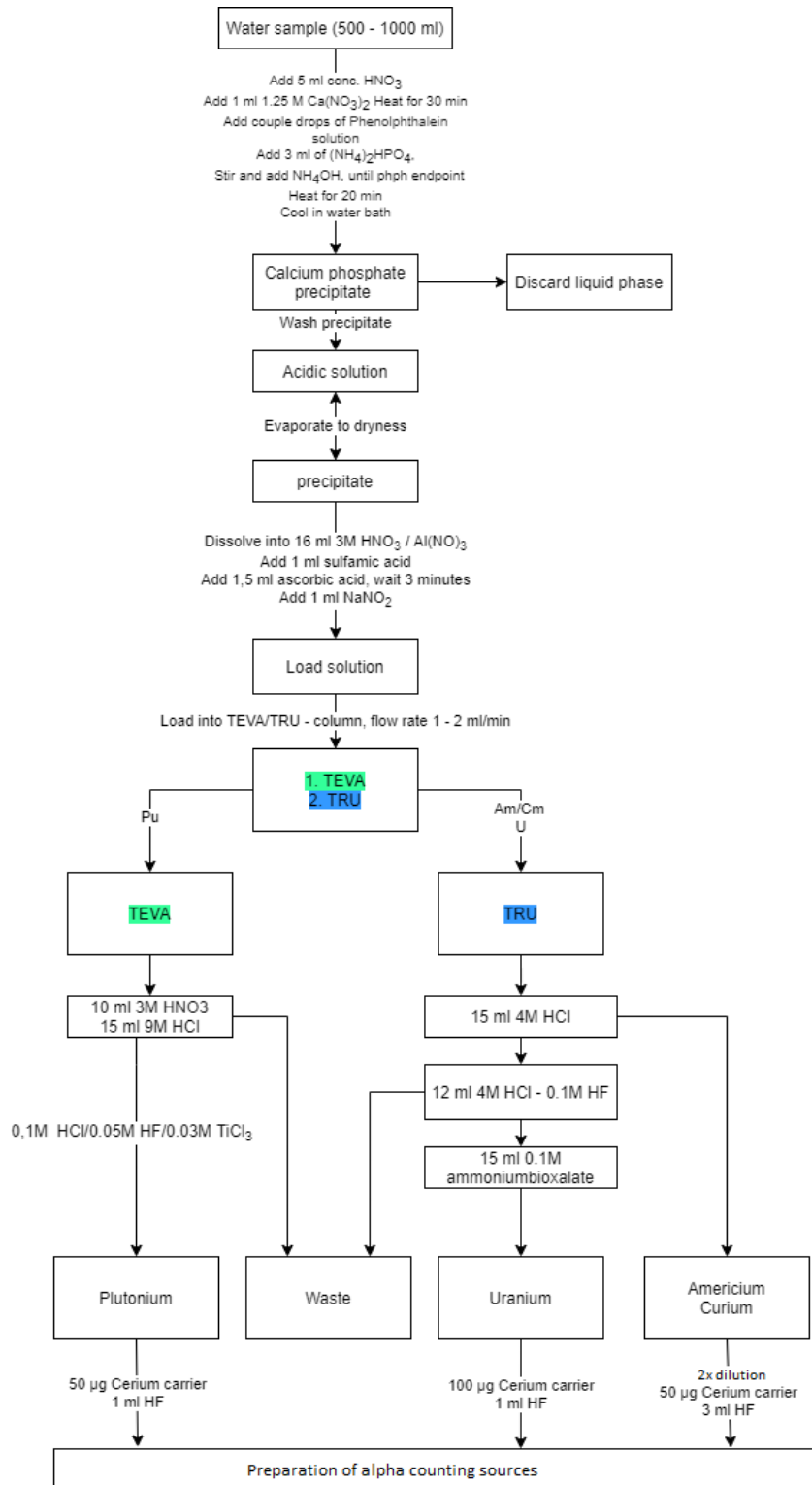
Appendix 1.4. Effect of eluant properties on UTEVA and TEVA k'



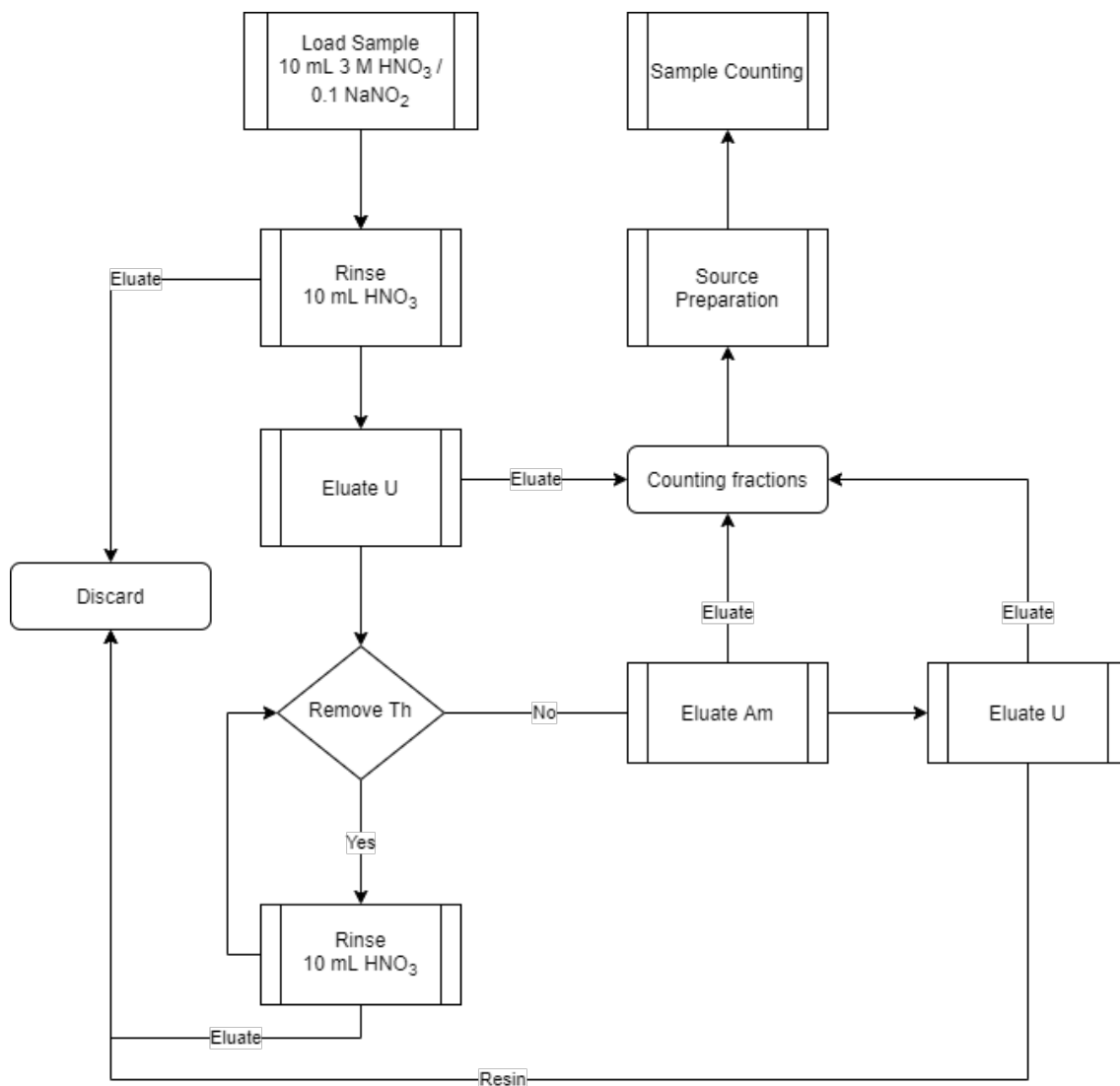
Change in k' in with varying HCl and HNO_3 concentrations for various ions in TEVA (left) and UTEVA (right)

Data from [21], [22], [79], [80]

Appendix 2. Separation scheme, EICHRUM



Appendix 3. Separation scheme, DGA



Appendix 4. Result sheet, Alpha-Apex

Alpha Spectrum Analysis Report

25.2.2020 7:50:38

Page 1

 ***** A L P H A S P E C T R U M A N A L Y S I S *****

Sample Title: Unknown #2 U
 Spectrum Description: Administrator
 Sample Identification: Unknown #2 U
 Sample Type:
 Sample Geometry: Shelf 3

Spectrum File: C:\Canberra\ApexAlpha\Root\Data\0000002
 Env. Background File: C:\Canberra\ApexAlpha\Root\Data\0000002
 Reagent Blank File: <not performed>

Sample Size: 0.535 L
 Sample Date/Time: 18.2.2020 12:00:36
 Acquisition Date/Time: 19.2.2020 15:13:19
 Acquisition Live Time: 417600.0 seconds
 Acquisition Real Time: 417601.7 seconds

Tracer Certificate File: C:\Canberra\ApexAlpha\Root\Certificates
 Tracer Quantity: 0.147 mL
 Effective Efficiency: 0.1160 +/- 0.0023
 Counting Efficiency: 0.1275 +/- 0.0031 on 16.1.2020 14:38:43
 Chem. Recovery Factor: 0.9095 +/- 3.16%

Peak Match Tolerance: 0.100 MeV

 ----- PEAK AREA REPORT -----

| Nuclide | Energy (MeV) | Net Pk Area | Pk Area Error % | Ambient Backgnd | Reagent Backgnd | FWHM (keV) |
|---------|--------------|-------------|-----------------|-----------------|-----------------|------------|
| U232 | T 5.262 | 3275.13 | 1.75 | 3.87 | 0.00 | 53.4 |
| U-234 | 4.703 | 5.13 | 69.53 | 3.87 | 0.00 | 2.9 |
| U-235 | 4.312 | 2.07 | 117.22 | 1.93 | 0.00 | 2.9 |
| U-238 | 4.155 | 9.00 | 33.33 | 0.00 | 0.00 | 2.9 |

T = Tracer Peak used for Effective Efficiency

 ----- NUCLIDE ACTIVITY REPORT -----

| Nuclide | Activity (dpm/L) | Activity Error % | MDA (dpm/L) | MDA Error % |
|---------|------------------|------------------|-------------|-------------|
| U232 | 7.595 | 2.02 | 0.027 | 2.02 |
| U-234 | 0.012 | 69.56 | 0.027 | 2.02 |
| U-235 | 0.006 | 117.24 | 0.026 | 2.02 |
| U-238 | 0.021 | 33.39 | 0.006 | 2.02 |