Production and Evaluation of $^{236g}$Np and Reference Materials for Naturally Occurring Radioactive Materials

THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF ENGINEERING
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Abstract

This thesis is based on the development of a radiochemical separation scheme capable of separating both $^{236}\text{g} \text{Np}$ and $^{236}\text{Pu}$ from a uranium target of natural isotopic composition (~1 g uranium) and ~200 MBq of fission decay products. The isobaric distribution of fission residues produced following the bombardment of a natural uranium target with a beam of 25 MeV protons has been evaluated. Decay analysis of thirteen isobarically distinct fission residues were carried out using high-resolution $\gamma$-ray spectrometry at the UK National Physical Laboratory. Stoichiometric abundances were calculated via the determination of absolute activity concentrations associated with the longest-lived members of each isobaric chain. This technique was validated by computational modelling of likely sequential decay processes through an isobaric decay chain. The results were largely in agreement with previously published values for neutron bombardments on natural uranium at energies of 14 MeV. Higher relative yields of products with mass numbers $A\sim110–130$ were found, consistent with the increasing yield of these radionuclides as the bombarding energy is increased. Using literature values for the production cross-section for fusion of protons with uranium targets, it is estimated that an upper limit of approximately 250 Bq of activity from the $^{236}\text{Np}$ ground state was produced in this experiment. Using a radiochemical separation scheme, Np and Pu fractions were separated from the produced fission decay products, with analyses of the target-based final reaction products made using Inductively Couple Plasma Mass Spectrometry (ICP-MS) and high-resolution $\alpha$ and $\gamma$-ray spectrometry. In a separate research theme, reliable measurement of Naturally Occurring Radioactive Materials is of significance in order to comply with environmental regulations and for radiological protection purposes. The thesis describes the standardisation of three reference materials, namely Sand, Tuff and TiO$_2$ which can serve as quality control materials to achieve traceability, method validation and instrument calibration. The sample preparation, material characterization via $\gamma$, $\alpha$ and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and the assignment of values for both the $4n$ Thorium and $4n + 2$ Uranium decay series are presented.
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Chapter 1

1. Introduction and Project Background

1.1 Introduction

Radioactivity measurement standards differ from those of other physical quantities in that the activity is stochastic in nature and the standards themselves are transient (due the process of radioactive decay). Additionally, there is no single physical standard which can act as a reference for all activity measurements and no single detector system or technique which can be used to standardise all radionuclides. National Measurement Institutes (NMIs) under the guise of the Bureau International des Poids et Mesures (BIPM), hold the highest-level (primary) measurement standards of radionuclides at a national level and disseminate them via accredited calibration laboratories to lower level users within the national measurement infrastructure (Figure 1.1).

![Figure 1.1 - Schematic of the International Metrology Infrastructure (npl.co.uk).]
Typically, this dissemination is performed by the supply of accurately weighed aliquots of the aqueous solution used in the production of the primary standard (Keightley, et al, 2015).

The ultimate purpose of the work presented in this thesis is to support this infrastructure by developing techniques to produce a standard solution of $^{236}\text{Np}$ to suitably quantify $^{237}\text{Np}$, and, in addition having a series of reference standards that can be used to ensure traceable measurements of NORM materials, in the secondary measurement technique of $\gamma$-ray spectrometry.

1.1.1 National Physical Laboratory
The National Physical Laboratory (NPL) is the UK’s NMI. Established in 1900 it provides, develops and maintains the UK’s measurement infrastructure that underpins the UK’s prosperity and quality of life (NPL Annual Review, 2015). It maintains traceability (Figure 1.1) ensuring accurate and consistent metrology in the following sectors:

- Advanced Manufacturing
- Defence & Security
- Digital economy
- Energy
- Healthcare

1.2 Project Background
1.2.1 Motivation to study $^{236}\text{Np}$
Edwin McMillan and Phillip H. Abelson first identified the element neptunium (Np) in 1940 (McMillan and Abelson, 1940) at the Berkeley Radiation Laboratory, University of California. A layer of uranium trioxide was exposed to secondary moderated slow neutrons from a
cyclotron, resulting in the fusion of the reactants (rather than fission) forming two new radioactive components. One component with a 23-minute half-life, was later found to be $^{239}\text{U}$, and the second with a half-life of 2.356 days was found to originate from the decay of $^{239}\text{Np}$.

This work had been preceded by the work of Emilio Segrè who had irradiated uranium with slow neutrons, and was thought to have produced a variety of new elements. As Segrè (1939) quoted;

“the necessary conclusion seems to be that the 23-minute uranium decays into a very long-lived element 93 and that transuranic elements have not yet been observed.”

Segrè noted this contradictory statement in his paper, and outlined the lack of observation of any alpha decay activity that would emanate from the daughter product following the beta decay of this new material with an atomic number 93. It was this work by Segrè (1939) that led McMillan and Abelson to revisit the chemical analysis and determine its properties in greater depth. They were able to show chemically that the end result was $^{239}\text{Np}$, a transuranic element with a half-life of 2.356 days (Browne and Tuli, 2013).

$$^{238}\text{U} (n, \gamma) ^{239}\text{U}_\beta^- + \bar{\nu}_e \rightarrow ^{239}\text{Np} \ (Equation \ 1.1)$$

Of the isotopes (Thakur and Mulholland, 2012) of neptunium identified to date, which range from $A = 225$ to $244$, the longest lived is $^{237}\text{Np}$ with a half-life of $2.144 \times 10^6$ years (Basunia, 2006). Measurements of $^{237}\text{Np}$, are of importance in a number of fields including nuclear forensics, environmental analysis, decommissioning and measurements throughout the nuclear fuel cycle. However, the measurement of $^{237}\text{Np}$ is complicated due to its low specific activity.
1562 ± 7 Bq per µg (Brauer, et al, 1960) and also the lack of suitable chemical yield tracer (Kalmykov, 2004; Jerome, et al, 2014). Radiometric techniques such as α-particle spectrometry (Yamamoto, et al, 1989) and liquid scintillation counting have traditionally been carried out to determine $^{237}$Np activity concentrations in the environment encompassing both a combination of weapons fall out and nuclear fuel waste.

Due to long counting times and time consuming laboratory procedures, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Nygren and Rodushkin, 1996; Scott, et al, 1991) techniques for neptunium measurement have become more widely used. ICP-MS offers simultaneous multi-element analysis providing information on the isotopic composition for a wide range of elements, as well as a rapid analysis compared with traditional alpha spectrometry. However, the chemical separation processes involved in removing heavy elements, in particular the separation of uranium to avoid the interference from the down mass tailing of $^{238}$U using ICP-MS (Kim, et al, 1989), are complicated. Therefore, a suitable elemental tracer is required to monitor radiochemical yield and ensure acceptable uncertainties in the analysis (Riglet, et al, 1992).

1.2.2 Aims of research

This thesis has a primary focus on the study of synthesis, separation and evaluation of the decay of the actinide radionuclide $^{236}$Np. Neptunium-236 is the ideal candidate for a neptunium yield tracer, as its relatively long half-life of 1.55(8) × 10$^5$ years (Chechev and Kuzmenko, 2012a) means that it is useable in both radiometric and mass spectrometric measurements (Jerome, et al, 2014). The thesis will also provide an evaluation of the mass distribution of the fission fragment decay residues from 25 MeV proton-induced fission in competition with $^{236}$Np production. These were produced following proton bombardment on a natural uranium target.
and provides initial yield data, which is of potential importance in the evaluation of the effectiveness of the chemical separation techniques utilised to isolate the $^{236}\text{Np}$ material in the process.

In a separate research theme, discussed in Chapter 5, an assessment has been carried out on the standardisation and characterisation of Naturally Occurring Radioactive Materials (NORMs), as part of a European wide research project, funded through the European Metrology Research Programme (EMRP).

1.2.3 European Metrology Research Programme

The European Metrology Research Programme (EMRP) is a programme of research supported by the European Association of National Metrology Institutes (EURAMET) and the European Commission. It is to ensure growing efforts of collaboration between member countries, increasing impact and ensuring that duplication does not occur between research carried out by member states. One such project is that of MetroNORM (IND57, Metrology of NORM), of which some of the work carried out is presented in this thesis.

1.2.4 Background to the UK Nuclear Industry and relevant to Np waste evaluation

Nuclear power stations have been in operation since 1956. The UK currently has 15 reactors at eight sites, with all but one to be retired by 2023 (NDA, 2016). Of these 15 reactors, 14 are advanced gas-cooled reactors (AGR) and one is a pressurised water reactor (PWR).
1.2.4.1 Magnox

Between 1956 and 1971 the first eight Magnox reactors were commissioned; these fleet of reactors were the first commercial power reactors to be built in the UK. More recently the reactor at Wylfa was the only reactor from the Magnox fleet that was still online, operating at around 590 MW (e) (Oka, 2014). The reactors are cooled by CO₂ and use (unenriched) natural uranium as fuel. The reactors have high fuel costs, a low power density, are reliable and have been in operation for the last 60 years.

1.2.4.2 Advanced gas-cooled reactors (AGR)

Seven AGR commercial stations were built between the 1970s and 1980s they were designed as the follow up to the Magnox reactors. Like the Magnox reactor, the AGR uses carbon dioxide as a coolant but incorporates uranium dioxide fuel pellets, inside stainless steel tubes to enable higher coolant pressures (~40 bar) and temperatures (outlet temperatures ~ 650°C) to be achieved (Oka, 2014). Coolant gas is circulated from the core to steam generators, mounted inside the pre-stressed concrete pressure vessel. The fuel is enriched to about 2.3% ²³⁵U to overcome the significant neutron absorption of the stainless-steel fuel cans. In addition, AGRs can be refuelled on load and the fuel can remain in the core for up to five years, with this design a much higher volumetric power density and fuel rating is possible when compared with Magnox reactors.

1.2.4.3 Pressurised water reactor (PWRs)

In a PWR, the water is used as a primary coolant and is pumped under high pressure to the reactor core where it is heated via the energy generated by the fission of heavy atomic nuclei of the elements of uranium and plutonium. The heated water then flows to a steam generator where it transfers its thermal energy to a secondary system where steam is generated and flows
to turbines which, in turn, spin an electric generator. Pressurized water reactors (Figure 1.2), like all thermal reactor designs, require the fast fission neutrons to be slowed down (a process called moderation or thermal) in order to interact with the nuclear fuel and sustain the chain reaction (Krane, 1998).

![Figure 1.2- Sizewell-B PWR Power station (NDA, 2016).](image)

In PWRs the coolant water is used as a neutron moderator. Fission and β^-delayed neutron collisions with the nuclei of the hydrogen atoms in the water, transfer kinetic energy in the process. This moderation of the neutron kinetic energies happens more efficiently when the water is further pressurised (i.e. the probability of collisions per unit volume travelled increases). The use of water as a moderator is an important safety feature of PWRs, as an increase in temperature may cause the water to expand, reducing the probability of thermalisation and reducing the extent to which neutrons are slowed down from energies of ~ MeV to thermal energies.
<table>
<thead>
<tr>
<th>Name of Plant</th>
<th>Reactor type</th>
<th>First power</th>
<th>Shut down date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dungeness B 1&amp;2</td>
<td>AGR</td>
<td>1983 &amp; 1985</td>
<td>2018</td>
</tr>
<tr>
<td>Hartlepool 1&amp;2</td>
<td>AGR</td>
<td>1983 &amp; 1984</td>
<td>2024</td>
</tr>
<tr>
<td>Heysham I-1 &amp; I-2</td>
<td>AGR</td>
<td>1983 &amp; 1984</td>
<td>2019</td>
</tr>
<tr>
<td>Heysham II-1 &amp; II-2</td>
<td>AGR</td>
<td>1988</td>
<td>2023</td>
</tr>
<tr>
<td>Hinkley Point B 1&amp;2</td>
<td>AGR</td>
<td>1976</td>
<td>2023</td>
</tr>
<tr>
<td>Hunterston B 1&amp;2</td>
<td>AGR</td>
<td>1976 &amp; 1977</td>
<td>2023</td>
</tr>
<tr>
<td>Torness 1&amp;2</td>
<td>AGR</td>
<td>1988 &amp; 1989</td>
<td>2023</td>
</tr>
<tr>
<td>Sizewell B</td>
<td>PWR</td>
<td>1995</td>
<td>2035</td>
</tr>
</tbody>
</table>

Table 1.1- Summary table of all current UK nuclear power plants (NDA, 2016).

1.2.5 Radioactive waste

The history of radioactive waste stems back to the 1920s (MacKee, 1921) where applications of X-rays and radium became prominent (Mould, 1993). What followed was the nuclear civil program of the 1950s, and the use of radioactivity in medicine and industry. Subsequently, the UK was a pioneer in the development of civil nuclear power with the commissioning in the 1960s of the first ‘Magnox’ power plants.

In 2016 there were reportedly 470,000 cubic metres (NDA, 2016) of radioactive waste scattered around the UK. There were 37 sites producing significant radioactive waste, and many smaller users of radioactive materials such as hospitals and industrial, educational and research establishments and military. All of these produce small quantities of radioactive waste that are not shown on the illustration in Figure 1.3.
Approximately 95% of the United Kingdom’s radioactive waste originates from the nuclear power industry (Defra, 2007). This waste occurs not only as a result of the production of
nuclear fuel but also from the operation of nuclear reactors, spent fuel reprocessing, research and development activities and decommissioning of old facilities.

Nuclear reactors also produce waste from the decay products from reactions on the uranium nuclear fuel that is used in the reactor; these can be divided broadly into either fission products or neutron activation products. A significant group of radionuclides within the radioactive waste management industry are isotopes of actinide elements - a series of chemically similar radioactive elements, with atomic numbers ranging from element 89 through to element 103. Naturally occurring uranium and thorium are both actinides, as are man-made artificially created isotopes of plutonium ($Z = 94$) and, significantly for the purposes of this thesis, neptunium ($Z = 93$).

**1.2.6 Neptunium isotopes of importance in the nuclear industry**

Of the isotopes of neptunium identified to date $^{237}\text{Np}$ is the longest-lived with ($T_{1/2} = 2.144 \times 10^6$ years (Basunia, 2006)). Neptunium-237 along with other transactinide isotopes such as plutonium and americium are present in the environment as a result of atmospheric nuclear weapons testing; in reprocessing facilities (Thakur, 2012) from the capture of neutrons by uranium isotopes in nuclear reactors; and nuclear accidents such as Chernobyl (Simsek, 2014). Each year, a 1,000-megawatt-electric pressurized-water reactor (PWR) can produce about 25 tonnes of spent fuel containing approximately 10-12 kilograms of $^{237}\text{Np}$ (Albright and Barbour, 2005). At the end of 2005, the world’s nuclear power reactors had produced almost 55 tonnes of $^{237}\text{Np}$, of which 1000 kg is found in the UK (Albright and Kramer, 2005). Overall based on current inventories annual production of $^{237}\text{Np}$ is estimated to be about three tonnes. Of this material between 1945 and 1980 it has been estimated that approximately 40 TBq ($1.1 \times 10^3$ Ci) of $^{237}\text{Np}$ were released into the environment (Beasley, *et al*, 1998).
1.2.7 Production of $^{237}$Np

$^{237}$Np is produced as a by-product of neutron irradiation and capture on uranium ($^{238}$U and $^{235}$U) in nuclear reactors. Neutron irradiation of $^{238}$U (fast neutron activation) and $^{235}$U (double activation) result in the following reactions that lead to the production of $^{237}$Np:

$$^{238}\text{U} (n, 2n) \rightarrow ^{237}\text{U} \rightarrow ^{237}\text{Np} (Equation \ 1.2)$$

$$^{235}\text{U} (n, \gamma) \rightarrow ^{236}\text{U} (n, \gamma) \rightarrow ^{237}\text{U} \rightarrow ^{237}\text{Np} (Equation \ 1.3)$$

$$^{238}\text{U} (n, \gamma) \rightarrow ^{239}\text{Np} \rightarrow ^{239}\text{Pu} (n, \gamma) \rightarrow ^{240}\text{Pu} \rightarrow ^{241}\text{Pu} \rightarrow ^{241}\text{Am} \rightarrow ^{237}\text{Np} (Equation \ 1.4)$$

Neptunium-237 is then produced directly by $\alpha$ decay of its parent $^{241}$Am. A list of the most significant ‘capture’ radionuclides can be found in Table 1.2.
<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Neutron number</th>
<th>Half-life</th>
<th>Main Decay mode</th>
<th>Principle Alpha decay energy (keV)</th>
<th>Characteristic γ-ray energy (keV)</th>
<th>γ-ray Emission Probability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{235}$U</td>
<td>143</td>
<td>$7.038 \times 10^8$ y</td>
<td>$\alpha$</td>
<td>4 397.8 (13)</td>
<td>185.715 (5)</td>
<td>57.2 (5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>143.764 (2)</td>
<td>10.96 (8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>163.358 (2)</td>
<td>5.08 (4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>205.309 (2)</td>
<td>5.01 (5)</td>
</tr>
<tr>
<td>$^{236}$U</td>
<td>144</td>
<td>$23.43 \times 10^6$ y</td>
<td>$\alpha$</td>
<td>4 494 (3) 4 445 (5)</td>
<td>49.46 (10)</td>
<td>0.081 (12)</td>
</tr>
<tr>
<td>$^{237}$U</td>
<td>145</td>
<td>$6.749 \times 10^3$ d</td>
<td>$\beta^-$</td>
<td>-</td>
<td>59.54091 (10)</td>
<td>34.1 (9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>208.00 (1)</td>
<td>21.3 (3)</td>
</tr>
<tr>
<td>$^{238}$U</td>
<td>146</td>
<td>$4.468 \times 10^9$ y</td>
<td>$\alpha$</td>
<td>4 198 (3) 4 151 (5)</td>
<td>49.55 (6)</td>
<td>0.063 (7)</td>
</tr>
<tr>
<td>$^{239}$U</td>
<td>147</td>
<td>$23.46 \times 10^5$ y</td>
<td>$\beta^-$</td>
<td>-</td>
<td>74.664 (1)</td>
<td>51.6 (13)</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>145</td>
<td>$24.1 \times 10^3$ y</td>
<td>$\alpha$</td>
<td>5 156.59 (14) 5 143.82 (21) 5 105.81 (21)</td>
<td>12.975 (10)</td>
<td>0.0341 (9)</td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td>146</td>
<td>$6.561 \times 10^3$ y</td>
<td>$\alpha$</td>
<td>5 168.13 (15) 5 123.6 (2)</td>
<td>45.244 (2)</td>
<td>0.0462 (9)</td>
</tr>
<tr>
<td>$^{241}$Pu</td>
<td>147</td>
<td>$14.33 \times 10^6$ y</td>
<td>$\beta^-$</td>
<td>4 897.3 (5)</td>
<td>148.567 (10)</td>
<td>0.0001863 (8)</td>
</tr>
<tr>
<td>$^{237}$Np</td>
<td>144</td>
<td>$2.144 \times 10^6$ y</td>
<td>$\alpha$</td>
<td>4 788.0 (9)</td>
<td>29.374 (20)</td>
<td>14.3 (6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>86.477 (10)</td>
<td>12.26 (12)</td>
</tr>
<tr>
<td>$^{239}$Np</td>
<td>146</td>
<td>$2.356 \times 10^6$ y</td>
<td>$\beta^-$</td>
<td>-</td>
<td>106.125 (2) 277.599 (1) 228.183 (1)</td>
<td>25.9 (3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>14.4 (1)</td>
<td>11.32 (22)</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>146</td>
<td>$432.6 \times 10^5$ y</td>
<td>$\alpha$</td>
<td>5 485.56 (12)</td>
<td>59.5409 (1) 26.3446 (2)</td>
<td>35.92 (17)</td>
</tr>
</tbody>
</table>

Table 1.2- A list of decay properties of $^{235,238}$U and minor actinides produced following neutron capture of these materials, found in typical nuclear fuel (data taken from ENSDF).
Neptunium isotopes heavier than $A = 237$ are unstable with respect to $\beta^-$ decay. $^{239}$Np can be produced by the irradiation of $^{238}$U the capture following reaction:

$$^{238}\text{U} (n, \gamma) \rightarrow ^{239}\text{U} \rightarrow ^{239}\text{Np} (Equation \ 1.4)$$

In addition, as noted by Peppard, et al, (1951) trace amounts of $^{239}$Np are found naturally in the environment from within uranium minerals, but due to its 2.3565 day half-life (Browne and Tuli, 2013), no significant equilibrium concentration can be reached and thus there is very little accumulation in the environment. $^{238}$Np ($T_{1/2} = 2.117(2)$ days) (Browne and Tuli, 2014) is not found naturally but can be synthesized in reactors via the thermal capture reaction:
The \( ^{236}\text{Np} \) \((n, \gamma)\) \( ^{237}\text{Np} \) (Equation 1.5)

The \( \beta^- \)-emitting isotope \( ^{239}\text{Np} \) is routinely used in radiochemical analysis; it can be obtained by milking a sample of \( ^{243}\text{Am} \), its \( \alpha \)-decay parent (Yoshida, \textit{et al}, 2006). This is however both time consuming and expensive to perform routinely. The neptunium isotopes with \( A < 237 \) can decay by electron capture or competing \( \beta^+ \) decay, while some of the lighter isotopes also have observed \( \alpha \)-decay branches (Basunia, 2006). \( ^{235}\text{Np} \) and \( ^{236}\text{Np} \) can be formed by proton/deuteron irradiation of \( ^{235}\text{U} \) and other uranium targets (Yoshida, \textit{et al}, 2006) and not directly by the irradiation of uranium with thermal neutrons, meaning they cannot be found in the environment but they can be used as a tracer for \( ^{237}\text{Np} \) analysis (Thakur, 2012).

1.2.8 \( ^{236}\text{Np} \) excited states/nuclear states

The ground state of \( ^{236}\text{Np} \), \( (^{236g}\text{Np}) \) is usually accompanied by the metastable state \( (^{236m}\text{Np}) \) when produced en masse, with the production ratio between \( ^{236m}\text{Np} \) and \( ^{236g}\text{Np} \) dependent on the incoming particle energy and resulting input angular momentum/excitation energy profile in a specific nuclear reaction. The ground state of this prolate deformed nucleus decays with a half-life of \( 1.55 \times 10^5 \) years (Browne and Tuli, 2006). The main metastable state has an evaluated decay half-life of 22.5 h (Browne and Tuli, 2006). Both states decay to excited states in \( ^{236}\text{U} \) (by electron capture) and \( ^{236}\text{Pu} \) (by \( \beta^- \)-decay) (Jerome, \textit{et al}, 2014) but can be identified by which excited states are populated in the \( ^{236}\text{U} \) and \( ^{236}\text{Pu} \) daughters. The \( ^{236}\text{Np} \) level scheme will be discussed in more detail in Chapter 6 of this thesis.

1.2.9 Why a \( ^{236g}\text{Np} \) tracer?

The procedures used in radiochemical separations are rarely fully quantitative, thus it is necessary that an accurate chemical yield is determined for the radionuclide of interest. A
suitable way to validate the concentration of the trace constituent is to determine the amount measured at the end of the process and the amount that was initially present in the original sample. In order to carry this out, it is necessary to have a way of monitoring the chemical recovery, which can be accomplished by the use of a radiochemical yield tracer (Efurd, 1991). The practical candidate neptunium isotopes that could be used as a yield tracer are $^{235}$Np, $^{236}$Np and $^{239}$Np. Of these only $^{236}$Np is suitable for mass spectrometry. $^{235}$Np ($T_{1/2} = 396.1$ days, Browne and Tuli, 2013) often contains $^{237}$Np as an impurity during its production which creates isobaric interferences as a result of the reaction to form the isotope, which involves proton irradiation of $^{236}$U. The relatively short half-life of $^{239}$Np ($T_{1/2} = 2.356$ days, Browne and Tuli, 2013) makes it unsuitable for use as a mass spectrometry tracer.
<table>
<thead>
<tr>
<th>Mass number (A)</th>
<th>Half-Life ($T_{1/2}$)</th>
<th>Main Decay Mode</th>
<th>Daughter Nucleus</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>235</td>
<td>396.1 d</td>
<td>EC &gt; 99%</td>
<td>$^{235}\text{U}$</td>
<td>E. Browne, J. K. Tuli: Nuclear Data Sheets 114, 751 (2013)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha$: 0.0026%</td>
<td>$^{231}\text{Pa}$</td>
<td></td>
</tr>
<tr>
<td>236$^{m}$</td>
<td>22.5 h</td>
<td>$\beta$: 50%</td>
<td>$^{236}\text{Pu}$</td>
<td>E. Browne, J. K. Tuli: Nuclear Data Sheets 107, 2649 (2006)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EC ~ 50%</td>
<td>$^{236}\text{U}$</td>
<td></td>
</tr>
<tr>
<td>236$^{g}$</td>
<td>$1.54 \times 10^5$ yr</td>
<td>EC ~ 87%</td>
<td>$^{236}\text{U}$</td>
<td>E. Browne, J. K. Tuli: Nuclear Data Sheets 107, 2649 (2006)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\beta$: 13%</td>
<td>$^{236}\text{Pu}$</td>
<td></td>
</tr>
<tr>
<td>237</td>
<td>$2.144 \times 10^6$ yr</td>
<td>$\alpha$: 100%</td>
<td>$^{233}\text{Pa}$</td>
<td>Balraj Singh, Jagdish K. Tuli: Nuclear Data Sheets 105, 109 (2005)</td>
</tr>
<tr>
<td>238</td>
<td>2.12 d</td>
<td>$\beta$</td>
<td>$^{238}\text{Pu}$</td>
<td>E. Browne, J. K. Tuli: Nuclear Data Sheets 127, 191 (2015)</td>
</tr>
<tr>
<td>239</td>
<td>2.36 d</td>
<td>$\beta$</td>
<td>$^{239}\text{Pu}$</td>
<td>E. Browne, J. K. Tuli: Nuclear Data Sheets 122, 293 (2014)</td>
</tr>
</tbody>
</table>

Table 1.3- Radioactive decay characteristics of neptunium isotopes of relevance to the current work.
Bearing in mind the difficulty of obtaining a neptunium chemical yield tracer and the data quality requirements for such measurements, although the aim of this thesis is to develop a \(^{236}\text{Np}\) tracer, in some instances it may be possible to employ a plutonium yield tracer, such as \(^{236}\text{Pu}\) (Maxwell, \textit{et al}, 2010\textsc{a}; Thakur and Mulholland, 2012). This approach is acceptable and has been successful for measurements where a higher level of uncertainty may be tolerated (Jerome, \textit{et al}, 2014). However, there is always the risk of fractionation neptunium and plutonium during analysis and this may be especially so in solid matrices (Jerome, \textit{et al}, 2014). For high-precision work involving \(^{237}\text{Np}\), including measurements for forensic purposes, it is therefore essential that the tracer is a neptunium isotope.

Since 2012, as part of the National Physical Laboratory’s work to maintain regular supplies of \(^{236}\text{Pu}\), proton irradiation of \(^{235}\text{U}, ^{236}\text{U}\) and \(^{238}\text{U}\) targets has been carried out at the University of Birmingham cyclotron (Jerome, \textit{et al}, 2012). The main focus of this is to investigate the metrology of civilian nuclear waste and to evaluate the processes for the production of a \(^{236}\text{Np}\) standard source, which is isobarically and chemically isolated from other transactinide and residual fission fragment residues.

\section*{1.2.10 Naturally Occurring Radioactive Materials}

As discussed in section 1.2.2, a separate but related measurement project was conducted on the standardisation and characterisation of naturally occurring actinide radioactive materials. There are two main sub-groups of radioactive nuclides in the environment: (a) naturally occurring and (b) man-made. The previous section focused on the occurrence of nuclear waste from the UK civil nuclear programme, however wastes generated from the nuclear supply chain can also contain Naturally Occurring Radioactive Materials (NORM) (Kathren, 1998). These are found naturally in the wider environment but can also be found in industrial activities such as:
• Coal industry (mining and combustion) (Mishra, 2004)

• Oil and gas industry (production) (Garner, 2015)

• Fracking (Diwekar, 2015)

• Metal mining and smelting (Falck, 2015)

• Mineral sands (rare earth minerals, titanium and zirconium) (Chang, et al, 2008)

• Fertiliser (phosphate) industry (Aoun, 2012)

• Building industry, cement production (Maringer, et al, 2013)

• TiO₂ pigment production (Mantero, et al, 2012)

In processes where U, Th and K concentrations of NORM have been increased by human industrial activity, the materials may be called Technologically-Enhanced Naturally Occurring Radioactive Materials (TENORM) (Kathren, 1998; Shakhshow, et al, 2011). These wastes can carry a significant economic and ecological burden (IAEA, 2011) if they are not properly disposed of and pose a potential health hazard to the general public. Exposure to naturally occurring radiation is responsible for the majority of an average person’s yearly radiation dose. In the UK, Public Health England has calculated that on average people are exposed to about 2.7 millisieverts (mSv) of ionising radiation per year (PHE, 2013). The waste produced in TENORM industries must be identified and measured in a traceable way by a National Measurement Institute (NMI), with calibration standards and reference materials that are adapted in an appropriate manner to the real composition and geometry of measured materials.
1.2.11 Why produce reference materials?

There is a general need for solid reference materials associated with environmental radioactivity to serve as quality control materials to achieve traceability, method validation and instrument calibration (Harms and Gilligan, 2012). There are two main types of reference materials: either characterised (real) contaminated samples (Shakhashiro, et al, 2011; Merešová, et al, 2012a) or simplified matrices spiked with known activities (Harms and Gilligan, 2012). Traceability of the latter is much more direct (Jerome, et al, 1994) however the compromise is that the matrix is often different in terms of composition and density from real contaminated samples. NPL as the UK National Metrology Institute creates reference materials, on an annual basis as part of its Environmental Proficiency Exercises. These exercises help analysts to identify measurement problems and support the UKAS accreditations in this area; they are run on an annual basis and the use of characterised real materials is generally preferred by the UK user community (Harms and Gilligan, 2012). Thus as part of this research thesis, three reference materials have been characterised and certificated as part of the European Metrology Research Project (JRP IND 57) MetroNORM.

1.2.12 Structure of thesis

Chapter 2 provides a review of the theoretical aspects of nuclear physics including radioactive decay modes, energetics and angular momentum/parity selection rules of associated with alpha, beta decay and γ-ray emission. It also provides an overview of nuclear reaction production rates and principles of nuclear fission. Chapter 3 discusses the fundamental principles of radiochemistry including: radiotracers, background on chemical separation techniques and redox chemistry that underpin the radiochemistry that are utilised in the study. Chapter 4 provides an overview of the metrology techniques used in the work, and aspects of radiation interaction with matter, semi-conductors, and radiation detection. Chapters 5 and 6 provide an
overview of the production of the NORM reference materials and the purification of $^{236}$Np respectively. Chapter 6 also includes a discussion on the low-lying nuclear structure of $^{236}$Np and its characteristic decay signatures from its ground state and long-lived metastable state. Finally, Chapter 7 outlines the conclusions of the thesis, with a short discussion on potential further work.
Chapter 2

2. Theoretical Background

In this chapter the physics and theory which underpin nuclear decay and radioactivity in terms of governing the production and decay of radioactive materials will be presented. This will include a discussion of nuclear binding energies and masses, main modes of radioactive decay (\(\alpha\) and \(\beta\)), electromagnetic decay processes (characteristic X-rays and \(\gamma\) rays) and nuclear reaction energetics.

Experiments conducted by Rutherford, Geiger and Marsden based on scattering of charged particles suggested that the atomic nucleus consists of a combination of protons (\(Z\)) and neutrons (\(N\)) and that a specific nuclear species is characterised by the total amount of positive charge in the nucleus and by its total number of mass units (Rutherford, 1911; Geiger and E. Marsden, 1913). Thus \(Z\) defines the nuclear charge and the element (i.e. the number of protons in the atomic nucleus), the neutron number, \(N\), defines the isotope of a given element.

2.1 Nuclear binding energy

Precise measurements of nuclear masses are needed in order to determine information on some of the most basic nuclear decay properties. Physical techniques such as mass spectrometry or energy balance in nuclear reactions allow for the determination of the masses of atoms of a particular \(Z\) and \(A\) (Lunney, et al, 2003). Isotopes, discovered by Soddy (1912) are atoms which nuclei have the same nuclear charge (+ Ze), but are physically distinguishable as they have different total nucleon/mass numbers \(A\).
The binding energy ($B$) of a nucleus is the difference in mass energy between a nucleus and its constituent $Z$ protons and $N$ neutrons; this corresponds to the energy required to break a nucleus up into its constituent nucleonic parts. The total mass energy can be written as (Lunney, et al, 2003; Wang, et al, 2012):

$$B = [Zm(^1H) + Nm_n - m(^1X)]c^2 \quad (Equation \ 2.1)$$

where $m(^1X)$ is the atomic mass of the system, including the atomic electrons and $m(^1H)$ is the mass of the hydrogen atom.

The underlying principles and gross features of nuclear binding energy can be modelled using the semi-empirical mass formula. First proposed by Von Weizsäcker (1935) the formula assumes that the nucleus acts in a way analogous to a ‘liquid drop of nuclear fluid’ and the total binding energy is expressed as a sum of five terms (Von Weizsäcker, 1935):

$$B = a_vA - a_sA^{2/3} - a_c\frac{Z^2}{A^{1/3}} - a_a\frac{(N-Z)^2}{A} \pm \Delta \quad (Equation \ 2.2)$$

where $a_v$, $a_s$, $a_c$, $a_a$ and $\Delta$ are constants obtained by fitting formula to experimentally determined values of masses and binding energies. The five terms can be expressed as volume, surface, coulomb, symmetry and pairing effects respectively.

- **Volume energy ($a_vA$):** The binding energy per nucleon is assumed to be approximately constant, which is consistent with the idea that each nucleon attracts only its closer neighbour strongly. The binding energy is proportional to $A$, indicating a constant nuclear density and the short range native of the strong nuclear force.
- **Surface correction (- $a_s A^{2/3}$):** Nucleons closest to the nuclear surface have fewer nucleons to bind with, thus creating a reduced level of total nuclear binding energy. Thus the surface area is proportional to $A^{2/3}$ and this term must be subtracted from the volume term to correct for this.

- **Coulomb energy (- $a_c \frac{Z^2}{A^{1/3}}$):** The binding energy of the nucleus must be reduced by the coulomb repulsion between positively charged protons within the nucleus. This value of the $a_c$ constant can be calculated to be $0.72 \text{ MeV}$ with $R_0 = 1.2 \text{ fm}$.

- **Symmetry term - $a_a \frac{(N-Z)^2}{A}$:** The form of the symmetry is determined from the Pauli Principle: empirically it is found that for nuclei with $A \leq 40$, the stable nuclides have $Z \approx N$, while for heavier nuclides, the term is less important due to the increase in the Coulomb repulsion term requires additional neutrons for nuclear stability. The term also effects the sequential filling of individual nuclear states due to the fermionic nature of protons and neutrons.

- **Pairing $\Delta$:** The final term in the SEMF considers the additional binding energy produced by the spin pairing of nucleons. For odd number of total nucleons (odd $Z$ and even $N$, or even $Z$ and odd $N$), this term is not set to zero. The pairing contribution is positive, thus adding to the binding energy when $N$ and $Z$ are both even, and is negative if both $N$ and $Z$ are odd.

### 2.2 Energetics of nuclear reactions

Consider the nuclear reaction; written schematically as:

$$a + X \rightarrow b + Y \ (Equation \ 2.3)$$
where \( a \) is a projectile which is incident on stationary target \( X \), \( b \) the ejectile and \( Y \) being the residue (Krane, 1998). The Q-value of the reaction is defined as the initial total mass energy minus the final mass energy in the reaction, such that:

\[
Q = (m_{\text{initial}} - m_{\text{final}}) c^2 = (m_X + m_a - m_Y - m_b) c^2 \quad (\text{Equation 2.4})
\]

Q-values can be positive (exothermic) or negative (endothermic). For exothermic reactions the nuclear binding energy can be released as kinetic energy in the final products.

### 2.3 Radioactivity decay

Radioactivity decay is statistical in nature thus it is impossible to predict at what instance any given atom will disintegrate. The decay of a radionuclide may proceed either via a single process or through various competing decay modes and the relative probabilities of these competitive modes are specified by their branching ratios. The process that allows unstable nuclides to form isotopes which are more energetically favourable systems in terms of overall binding energy is called radioactive decay.

The rate of decay of a given source is given by the law of radioactive decay. If \( N \) radioactive nuclei are present at time \( t \) and if no new nuclei are introduced into the sample, then the number \( dN \) decaying in a time \( dt \) is proportional to \( N \), and thus:

\[
\lambda = -\frac{(dN/dt)}{N} \quad (\text{Equation 2.5})
\]
Here $\lambda$ is the decay constant and \(-\frac{dN/dt}{N}\) is the probability per unit time for the decay of an atom. The fact that this is a constant is the basic assumption of the statistical theory of radioactive decay.

The term radioactivity refers to the emission of ionising radiation or particles caused by these spontaneous nuclear transitions, which may emanate either from the nucleus itself or via interactions of the nucleus with atomic electrons. The rate of decay of a radionuclide is referred to as its activity $A$, and the activity of an amount of a radionuclide in a specified energy state at a given time is the expectation value, at that time, of the number of spontaneous nuclear transitions in unit time from that energy state, i.e.,

$$A(t) = \lambda N(t) = -\frac{dN}{dt} \quad (Equation \ 2.6)$$

The becquerel (symbol Bq), is the unit for the activity of a quantity of a radionuclide in which one nucleus decays per second, and thus in terms of the SI base units, is 1 reciprocal second ($s^{-1}$).

Assuming that $N_0$ atoms of the parent are present at $t = 0$ and no additional decay products are subsequently introduced then:

$$N_1 (t = 0) = N_0$$

$$N_2 (t = 0) = N_3 (t = 0) = ... = 0$$
The most common form of radioactive decay is where the parent nuclei only decay into a single
daughter nuclide species. Then the number of parent nuclei decreases as a function of time,
given by:

\[ dN_1 = -\lambda_1 N_1 dt \]  \( (Equation \ 2.7) \)

Integrating Equation 2.7, the exponential law of radioactive decay is derived:

\[ N(t) = N_0 e^{-\lambda t} \]  \( (Equation \ 2.8) \)

where \( N_0 \), the constant of integration, gives the original number of nuclei present at \( t = 0 \).
The half-life \( T_{1/2} \) defines the time taken for the number of radioactive atoms in the sample, \( N \),
to have taken to one half of the original value \( N_0 \), i.e. the time taken \( (t) \) at which:

\[ N(t) = \frac{N_0}{2} = N_0 e^{-\lambda T_{1/2}} \]  \( (Equation \ 2.9) \)

2.4 Sequential Decay

The daughter nuclides are created following the decay of the parent nuclide. However, if the
daughter nuclide is also radioactive, then due to the decay to the granddaughter nuclide, the
daughter nuclide population follows this differential form (Krane, 1998):

Where: \( \lambda_1 \) = decay constant of initial radionuclide species.

\( \lambda_2 \) = decay constant of 1st daughter radionuclide species.

\[ dN_2 = \lambda_1 N_1 dt - \lambda_2 N_2 dt \]  \( (Equation \ 2.10) \)
Solving this 1st order differential equation for \( N(2) \) as a function of time, one can derive the general expression for the number of nuclei present at time \( t \) of type \( N_2 \).

The solution to the equation is given by:

\[
N_2(t) = \frac{N_0 \lambda_1}{\lambda_2 - \lambda_1} \left( e^{-\lambda_1 t} - e^{-\lambda_2 t} \right) \quad (Equation 2.1)
\]

and therefore \( A_2 = \lambda_2 N_1 = \frac{\lambda_3 \lambda_2 N_0}{\lambda_2 - \lambda_1} \left( e^{-\lambda_1 t} - e^{-\lambda_2 t} \right) \)

2.5 The Bateman Equations

Bateman (1910) showed that by applying these equations to a chain of decays, it is possible to determine the population of each isotope in a decay chain at a time \( t \), using generalised solutions to these coupled differential equations. If \( N_{i-1}(0) \) is the number of atoms of the \( i \)th isotope of the series at time \( t = 0 \) and assuming zero concentrations of all daughters at time zero (Cetnar, 2006), then:

\[
N_i(0) \neq 0 \text{ and } N_i(0) = 0 \text{ when } i > 1 \quad (Equation 2.12)
\]

Therefore, the Bateman equation takes the general form (Bateman, 1910):

\[
N_1(t) = \lambda_1 \lambda_2 ... \lambda_{i-1} N_1(0) \sum_{j=1}^{i-1} e^{-\lambda_j t} \prod_{k \neq j}(\lambda_k - \lambda_j) \quad (Equation 2.13)
\]

Applying the Bateman equation for the second and third isotope in a decay series gives:
\[ N_2(t) = \frac{\lambda_1 N_1(0)}{\Delta \lambda_2} \left( e^{-\lambda_1 t} + e^{-\lambda_2 t} \right) \]

and

\[ A_2(t) = \frac{\lambda_2 N_2(t)}{\Delta \lambda_2} = \frac{\lambda_2 N_1(0)}{\Delta \lambda_2} \left( e^{-\lambda_1 t} - e^{-\lambda_2 t} \right) \] (Equation 2.14)

\[ = A_1(0) \frac{1}{1 - \lambda_2} \left( e^{-\lambda_1 t} - e^{-\lambda_2 t} \right) = A_1(t) \frac{\lambda_2}{\Delta \lambda_2} (1 - e^{-(\lambda_2 - \lambda_1)t}) \]

\[ N_3(t) = \frac{\lambda_1 \lambda_2 N_1(0)}{\Delta \lambda_2} \left( e^{-\lambda_3 t} + \frac{e^{-\lambda_2 t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)} + \frac{e^{-\lambda_3 t}}{(\lambda_3 - \lambda_2)(\lambda_3 - \lambda_1)} \right) \]

\[ A_3(t) = \lambda_3 N_3(t) = \lambda_2 \lambda_3 A_1(t) \left( e^{-\lambda_3 t} + \frac{e^{-\lambda_2 t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)} + \frac{e^{-\lambda_3 t}}{(\lambda_3 - \lambda_2)(\lambda_3 - \lambda_1)} \right) \]

\[ = \lambda_3 \lambda_2 A_1(t) \left[ \frac{1}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)} + \frac{e^{-(\lambda_2 - \lambda_1)t}}{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2)} + \frac{e^{-(\lambda_3 - \lambda_1)t}}{(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)} \right] \]

2.6 Radioactive Equilibrium

The quantitative relationship between the various members of a decay series is associated with half-life of the parent and its daughter. Thus the radioactivity of a particular radionuclide in a decay chain can be estimated by understanding its state of equilibrium.

There are three types of radioactive equilibrium: at the long-time limit; (a) no equilibrium, (b) transient equilibrium; and (c) secular equilibrium.

2.6.1 No Equilibrium

In examples, such as \(^{241}\text{Am}\) (\(T_{1/2} = 432.6\) (6) years, (Browne and Tuli, 2013)) where the parent nuclei have a much shorter half-life than its daughter \(^{237}\text{Np}\) (\(T_{1/2} = 2.144 \times 10^6\) years (Basunia, 2006)). In this example, no equilibrium is reached as the parent will decay away, leaving only the daughter nucleus in the sample.
Figure 2.1- Example of no equilibrium between the decay of $^{237}$Np ($T_{1/2} = 2.144 \times 10^6$ years) decaying into its $^{241}$Am ($T_{1/2} = 432.6$ years) daughter radionuclide, assuming a relative starting activity of 100 Bq at $A_0$.

Another example of this is from the $4n + 2$ Uranium series for the decay of $^{218}$Po ($T_{1/2} = 3.10$ mins) → $^{214}$Pb ($T_{1/2} = 26.8$ mins) (Wu, 2009), as shown in Figure 2.2.
Figure 2.2- Example of no equilibrium between the decay of $^{218}$Po ($T_{1/2} = 3.098$ mins) decaying into its ($^{214}$Pb $T_{1/2} = 26.8$ mins) daughter radionuclide assuming a relative starting activity of 100 Bq at $A_0$.

2.6.2 Transient Equilibrium

When assuming only the parent nucleus concentration is present at $t = 0$ and $N_2(t=0) = 0$, as the half-life of the parent is longer than that of the daughter radionuclide, when $t \rightarrow \infty$, the activity of the daughter $A_2$ reduces to (Krane, 1998):

$$A_2 = \frac{\lambda_2 A_1}{\lambda_2 - \lambda_1} \quad \text{(Equation 2.16)}$$

$A_2$ will increase until reaching a maximum value, and then will decrease at the same rate of its parent $A_1$. This is known as transient equilibrium. In the $^{232}$Th decay series $^{212}$Pb decays with a $T_{1/2} = 10$ hours to $^{212}$Bi with a $T_{1/2} = 60$ minutes (Figure 2.3), in this example the parent decays quickly and the daughter activity rises to a maximum and decays with its characteristic decay constant.
2.6.3 Secular Equilibrium

In this case the mean decay lifetime of the parent is longer than any of the daughters in the chain, thus $T_1 = \frac{1}{\lambda_1}$ is larger than the daughter $T_2 = \frac{1}{\lambda_2}$. This can be written as:

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \quad (Equation \ 2.17)$$

where $N_2$ is the change of concentration of the daughter with respect to time.

Solving $N_2$ (Thorne, 1987), gives:

$$A_2 = A_1 \left(1 - e^{\lambda_2 t} \right) + A_{2(t=0)} e^{-\lambda_2 t} \quad (Equation \ 2.18)$$

where at $t = 0$, $A_2 = 0$. The daughter nuclides activity then increases while the parent activity remains relatively constant due to its long half-life. In the example from the $4n + 2$ Uranium
series in Figure 2.4, $^{226}$Ra with a ($T_{1/2} = 1600$ (7) years) (Akovali, 1996), decays to its much shorter lived, ($T_{1/2} = 3.8231$ days) daughter $^{222}$Rn (Jain and Singh, 2006). Secular equilibrium occurs in each of the primordial decay chains, whereby the growth and decay of each isotope are equal, meaning that if one activity in the chain is measured it is assumed that that activity can be used to measure another radionuclide in that chain.

![Graph showing secular equilibrium from the decay of $^{226}$Ra to $^{222}$Rn](image)

Figure 2.4- Example of secular equilibrium from the decay of $^{226}$Ra ($T_{1/2} = 1600$ years) to $^{222}$Rn ($T_{1/2} = 3.8231$ days).

2.7 Modes of Radioactive Decay

2.7.1 Alpha decay

$\alpha$-decay occurs predominantly for heavy radionuclides with $Z$ greater than 83 (Gilmore and Hemingway, 2008) and involves the emission of doubly charged positive ions (or bare $^4$He nuclei). This is due to the $^4$He nucleus being a tightly bound system, which therefore allows the maximum release of kinetic energy for the mass of its constituent nucleons.
The process may be written schematically as:

\[ \frac{AX_N}{2} \rightarrow \frac{A-4}{2} X'_{N-2} + \alpha \quad (Equation \ 2.19) \]

where \( X \) is the chemical symbol of the parent radionuclide and \( X' \) is that of the daughter nuclide.

For a given transition, the total available energy \( Q \) is given by the fixed mass energy difference between the decaying and populated states of the initial and final nuclides respectively. \( \alpha \)-decay is an exothermic process as (i.e. \( Q_\alpha > 0 \)).

If \( m_p \) is the mass of the parent nucleus before \( \alpha \)-decay, \( m_D \) is the mass of the daughter nucleus formed in \( \alpha \)-decay, \( m_\alpha \) is the mass of the emitted \( \alpha \)-particle, \( E_D \) and \( E_\alpha \) are the kinetic energies of the daughter and \( \alpha \) particle, then the total energy released is given as:

\[
Q_\alpha = [m_p - m_D - m_\alpha]c^2 = E_D + E_\alpha \quad (Equation \ 2.20)
\]

For ground state to ground state \( \alpha \) decay, this total energy is released as the recoil kinetic energy to the nucleus and the \( \alpha \) particle, and is determined by the conservation of total linear momentum, which is zero, assuming the nucleus decays from rest. Thus, the daughter radionuclide must recoil in the opposite direction to the \( \alpha \)-particle and with the same linear momentum. Therefore, the ratio of the kinetic energies is then:

\[
\frac{E_D}{E_\alpha} = \frac{\frac{1}{2}m_Dv_D^2}{\frac{1}{2}m_\alpha v_\alpha^2} = \frac{(m_Dv_D)^2m_\alpha}{(m_\alpha v_\alpha)^2m_D} \quad (Equation \ 2.21)
\]
Thus, $E_\alpha$ and $E_D$ can be determined in terms of the $Q_\alpha$, $m_D$ and $m_\alpha$ by conservation of linear momentum, which leads to:

$$Q_\alpha = E_\alpha \left[ 1 + \frac{E_D}{E_\alpha} \right] = E_\alpha \left[ 1 + \frac{m_\alpha}{m_D} \right] \quad (Equation \ 2.22)$$

For heavy ($A > 200$) nuclei (Wang, et al, 2012) the majority of this energy (98%), is carried by the $\alpha$-particle. This is not to say that the 2% making up the recoil energy of the heavy fragment is to be dismissed. For a nuclide, such as $^{226}$Ra with a $Q$-value of 4.87 MeV, the recoiling nucleus has an energy of approximately 100 keV (Wang, et al, 2012), which is significantly in excess of the energy which binds atoms. However due to their relatively large mass and double positive charge, $\alpha$ particles lose energy rapidly in solid matter. For typical $\alpha$-particle energies of ~ 5 MeV, the mean path length in air at standard temperature and pressure is about 3.5 cm (Krane, 1998), and thus a thin coating placed over the radioactive sample can effectively trap the recoiling nuclei within ~ 10 µm (Krane, 1998). The energies of the emitted $\alpha$ decays are characteristic of the parent radionuclide can be used to identify a particular decaying species.

### 2.7.1.1 Alpha particle systematics

Alpha particles occur at energies that classically, would not be allowed to be emitted. Heavy nuclei such as $^{238}$U experience a Coulomb barrier for $\alpha$ particles in excess of 20 MeV (Rasmussen, 1965), with $\alpha$ particles emitted from uranium with energies of less than 5 MeV, ‘apparently violating energy conservation in the vicinity of the barrier’ (Lilley, 2001). A significant aspect of $\alpha$ decay as noticed by Geiger and Nuttall (1911) and in 1928 by Gamow, Gurney and Condon is that those $\alpha$ emitters with the highest $\alpha$ decay energies were also those with the shortest half-lives. For example:
$^{232}\text{Th} \ (T_{1/2} \sim 1.4 \times 10^{10} \text{ yrs}, Q = 4.08 \text{ MeV})$

$^{218}\text{Th} \ (T_{1/2} \sim 1.0 \times 10^{-7} \text{ s} \ Q = 9.85 \text{ MeV})$

These values show that a factor of two in energy means can result in a factor of $10^{24}$ in half-life (Geiger and Nuttall, 1928). This phenomenon has been explained by quantum mechanical tunnelling theory by the probability of an unbound $\alpha$ particle being able to tunnel through the coulomb potential barrier to exit the nucleus. Thus the narrower the width of the Coulomb barrier through which the $\alpha$ particle has to tunnel, the higher the probability of it being emitted; thus larger $Q$ values are linked to shorter $\alpha$-particle half-lives. This is shown diagrammatically in Figure 2.5 which shows an approximately linear relationship between log $T_{1/2}$ and $1/\sqrt{Q}$.

![Figure 2.5- Geiger-Nuttal plot showing the inverse relation between alpha-decay half-life and decay energy for even-even nuclei (Lilley, 2001).](image-url)
2.7.1.2 α particle energies fine structure and selection rules

The observed energies of α-particles emitted in radioactive decay from a particular parent radionuclide can often form a group of discrete peaks, named as fine structure. Having discussed conservation of total mass-energy and linear momentum, the final aspect of the α particle decay systematics is to discuss the nature of angular momentum and parity conservation in α decay. Total angular momentum must be conserved in α decay. For a transition from a nuclear state of angular momentum $I_i$ to a final daughter state of $I_f$, the orbital angular momentum carried by the α-particle with respect to the daughter nuclear can range from $I_i + I_f$ and $|I_i - I_f|$.

The intrinsic angular momentum/parity of the α-particles is of $I^π = 0^+$, based on 2 protons and 2 neutrons all being in a 1s orbital state, with spins coupled pairwise to spin/parity $0^+$. Thus, any angular momentum carried away in α particle emission must be due to the relative orbital angular momentum between the α particle and daughter nucleus, denoted by $I_α$. For even-even nuclei the ground states of each nuclei and associated α-particle all have a spin/parity of $0^+$.

2.7.2 Beta decay

Beta decay is a result of the weak nuclear force between nucleons and involves the transformation of a proton to a neutron, or a neutron to a proton; within the nucleus these can occur via the following schematic modes:

$$\frac{1}{2}X \rightarrow Z+1Y + e^- + \bar{v}_e \quad (β^-) \quad (Equation \ 2.23)$$

$$\frac{1}{2}X \rightarrow Z-1Y + e^+ + v_e \quad \quad (β^+) \quad (Equation \ 2.24)$$

$$\frac{1}{2}X + e^- \rightarrow Z+1Y + v_e + X_{ray} \quad (EC) \quad (Equation \ 2.25)$$
where $e^-, e^+, \nu_e$ and $\bar{\nu}_e$ are an electron, positron, electron-neutrino and an electron anti-neutrino respectively. $X$ and $Y$ represent nuclei with atomic number $Z$ and $Z + 1$ and total mass number $A$. In a nucleus, $\beta$ decay changes both the $Z$ and $N$ values by one unit, while the mass number $A$ is unchanged.

### 2.7.2.1 Energy release in $\beta$-decay

Energy release in $\beta$ decay is determined by the $Q$-value. In $\beta$ decay the daughter nucleus changes element from the mother, however unlike $\alpha$ decay, which is a two-body process, $\beta$ decay is a three-body process, producing an electron and (as postulated by Pauli in 1931), a second particle, later named by Fermi as the neutrino. There are two kinds of neutrino; the first is the anti-neutrino ($\bar{\nu}$), results from $\beta^-$ decay resulting from the transformation of a neutron to a proton. The second neutrino ($\nu$) is for neutron-deficient radionuclides, where $\beta^+$ decay is favoured and a positron and a neutrino are emitted, resulting from the transformation of a proton to a neutron. $\beta^+$ decay and electron capture (EC) are competing processes, electron capture occurs by capturing an orbital electron followed by the emission of a mono-energetic characteristic X-ray and mono-energetic neutrino.

The criterion for $\beta^-$ decay to be allowed energetically is that the initial total atomic mass exceeds the final atomic mass, since the mass of the electron emitted by the nucleus is compensated by the addition to the atom of an orbital electron, (due the unit increase in $Z$).

The $Q$-value for each of the three weak force decay modes can be given by the following (Krane, 1998):

$$Q_{\beta} = [m ({}^A X) - m ({}^A Y)] c^2 \quad (Equation \ 2.26)$$
\[ Q_{\beta^+} = [m(^{\alpha}X) - m(^{\beta}Y) - 2m_e] c^2 \] (Equation 2.27)

\[ Q_{EC} = [m(^{\alpha}X) - m(^{\beta}Y)] c^2 - B_n \] (Equation 2.28)

where \( m(Y), m(X) \) and \( B_n \) are the atomic masses of species \( Y \), atomic mass of species \( X \) and the binding energy of the captured \( n \)th shell electron respectively, these are tabulated in e.g. Audi. 
et al, 2012. This maximum end point energy in \( \beta^- \) is decay shared between the electron and the anti-neutrino, resulting in a continuous \( \beta^- \) particle energy spectrum, extending from zero to the maximum \( Q_{\beta^-} \)-energy.

The \( \beta^+ \) decay mode is only possible if the atomic mass of the parent is greater than that of the daughter by more than two electron rest masses i.e. \( Q_{\beta^+} > 2m_e = 1.022 \text{ MeV}/c^2 \). This is due to the fact that the parent atom loses one electron mass by the emission of a positron and another due to the decrease in atomic number resulting in a superfluous extra-nuclear electron.

In neutron-deficient radionuclides, where the difference between the initial and final energy states does not meet the above criteria required for \( \beta^+ \) decay, the parent radionuclide may still decay by electron capture. An example of this is the cosmogenic NORM radionuclide \(^7\text{Be} \), which decays 100\% by electron capture to \(^7\text{Li} \) and has no competing \( \beta^+ \) branch (Rubio and Gelletly, 2009). However, if the energy conditions for \( \beta^+ \) decay are met, then these two processes operate in direct competition (both yielding the same daughter nuclide). There are cases where in odd-odd nuclei both \( \beta^+ \) EC and \( \beta^- \) decay branches are energetically allowed, such as in naturally occurring \(^{40}\text{K} \). Considering the quantum mechanical behaviour of orbital atomic electrons, it is possible that they may actually enter the nucleus itself (being captured
in the process), and transform a proton into a neutron accompanied by the release of a mono-
energetic neutrino. This process is most likely for electrons from the inner-most or “K”-shell.
Electron capture occurs when an atomic shell creates a vacancy which is filled by electrons
from outer shells. The initial vacancy is transferred to the outer shell, which is subsequently
filled by the rearrangement of further orbital electrons. This cascade leads to the emission of
characteristic X-rays of the daughter element, with energies equal to the difference between
the binding energies of the shells containing and feeding the vacancies. Alternatively, some of
the available energy may be transferred directly to one or more of the outer shell electrons
resulting in their ejection from the atom (Auger electrons). The fluorescence yield for a
particular atomic shell (ϖ_K, ϖ_L, ϖ_M,...) is related to the ratio between these competing modes of
atomic de-excitation, and is defined as probability that the filling of a vacancy in that shell is
accompanied by the emission of the associated characteristic X-ray photon.

2.7.2.2 Mass difference

The difference in the total mass energy of nuclei and their constituent parts (protons and
neutrons) is the result of binding energy. Using the SEMF formula it is possible to examine the
gross features and relative stability of different nuclear species by evaluating the theoretical
trends for nuclear masses. Regions of experimentally identified neutron-rich and neutron-
deficient radioactive nuclei (compared to the lowest energy/mass isobar for a given A
value) are indicated on either side of the band of stable nuclei, the so-called valley of stability,
(Figure 2.6). The proton/neutron ratio for stability is approximately unity for \( Z \leq 20 \). For large
\( Z \), stable nuclei tend to exhibit a proton-neutron ratio that is less than unity, decreasing to
about two-thirds as \( Z \) increases to 83. Note that there are no stable isotopes for \( Z = 43 \) (Tc) or
\( Z = 61 \) (Pm). Comparing the mass of isotopes with the same atomic number (isobar) results in
the comparison of stability (taking the mass of proton to be approximately that of a neutron)
where the lowest mass occurs due to an increased binding energy (Figure 2.7).

For a fixed mass number \((A)\), the SEMF results in a parabolic (i.e. \(Z^2\)) dependence for binding
energy as a function of \(Z\) to the isotope with the lowest mass for a given isobaric chain, would
be expected to be the energetically most favourable combination of \(Z\) and \(N\). If \(A\) is an odd
integer, then a single parabola exists; however, with even \(A\) two parabolas co-exist, separated
in energy by \(2\Delta\), depending on whether the integer \(N\) and \(Z\) values are both even or odd. A
significant effect to note is that the \(\beta\) decay energy (which is the mass difference between two
consecutive isobars) increases the further away from the line of stability. When \(A\) is odd, it is
expected that only one isobar will be stable. For \(A\) even it is common to have two effectively
stable\(^1\) even-even isobars, as any odd-odd nuclide that intervene in the chain are greater than
either of the stable isobars. This leads to odd-odd nuclei such as \(^{40}\text{K}_{21}\) and \(^{236}\text{Np}_{143}\) decaying
in either direction, releasing energy by converting a proton into a neutron, or by converting a
neutron into a proton.

\(^1\) One of these is often unstable against double-\(\beta\)-decay to the other but the half-lives for such processes
are > \(10^{10}\) years
Figure 2.6- Stable and radioactive nuclei according to proton number $Z$ and neutron number $N \equiv (A - Z)$. Stable nuclei are indicated as black squares, while radioactive nuclei are indicated as shaded coloured squares (Figure taken from Lilley, 2001).
Figure 2.7- The black boxes represent stable nuclei on the line of stability, the yellow ones are proton rich nuclei and the blue one’s neutron rich nuclei. The red arrows indicate β decays possible between the radionuclide concerned. Fission products with \( A = 131 \) for example will form somewhere along the indicated diagonal and will β− decay following the arrows until they reach the stable nuclide \(^{131}\text{Xe}\) via the decay of \(^{131}\text{I}\) and its precursors (Figure and \( T_{1/2} \) values taken from DDEP).

### 2.7.2.3 Transition rules

Fermi in 1934 proposed a theory of β decay based on Pauli’s neutrino hypothesis that an electron (referring to electrons or positrons) and neutrino (referring to neutrino or anti-neutrino) do not exist before the decay process and are transformed from the initial nucleus state, and must be accounted for during the formation of those particles (Fermi, 1934). This implies that the initial nucleus state transforms into its final state plus an electron and neutrino (Dirac, 1927).

<table>
<thead>
<tr>
<th>Fission products with ( A = 131 )</th>
<th>( T_{1/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{131}\text{Cd})</td>
<td>68.00 ms</td>
</tr>
<tr>
<td>(^{131}\text{In})</td>
<td>0.28 s</td>
</tr>
<tr>
<td>(^{131}\text{Sn})</td>
<td>56.02 s</td>
</tr>
<tr>
<td>(^{131}\text{Sb})</td>
<td>23.03 m</td>
</tr>
<tr>
<td>(^{131}\text{Te})</td>
<td>25.00 m</td>
</tr>
<tr>
<td>(^{131}\text{I})</td>
<td>8.025 d</td>
</tr>
</tbody>
</table>
This can be calculated using Fermi’s Golden Rule for the transition rates of quantum systems by (Fermi, 1934):

$$\lambda = \frac{2\pi}{\hbar} |v_{fi}|^2 \rho(E_f) \quad (Equation \ 2.29)$$

$v_{fi}$ is the matrix element and $\rho(E_f)$ is the density of the available energy states. The Fermi Function $F(Z', p)$ where $p$ is the linear momentum of the electron and $Z'$ is number of protons in the daughter. The function also accounts for the influence of the nuclear Coulomb field.

$\beta$ decay is often shown and expressed by the total decay rate. The function $f(Z', E_0)$, known as the Fermi integral and $ft$ values where $T_{1/2}^f$ is the relevant half-life for that decay, includes all the information required for $\beta$-decay (Hodgson, 1997):

$$fT_{1/2} = 0.693 \frac{2\pi^3\hbar^7}{g^2m_2^2c^4|M_{fi}|^2} \quad (Equation \ 2.30)$$

$fT_{1/2}$ is what is known as the comparative half-life, allowing for a comparison of different $\beta$ decay probabilities in different nuclei. Formerly, $fT_{1/2}$ the values were used to classify transitions into named allowed transitions and forbidden transitions. Where “forbidden” here means rather suppressed compared to an allowed decay rather than strictly forbidden. By convention each transition can be defined as allowed, first forbidden, second forbidden...etc.
2.7.2.4 Angular momentum and parity selection rules

The energetics discussed so far assume that the $\beta$ decays are from the ground state of the mother nucleus direct to the ground state of the daughter nucleus. $\beta$ decay is also governed by spin and parity selection rules, where the allowed decays have angular momentum changes of $0$ or $\pm 1\hbar$.

Electrons and neutrinos both have half-integer intrinsic spins, $s = \frac{1}{2}$ and can be coupled together either parallel, totalling $S = I$, or anti-parallel, totalling $S = 0$. When the spins of the emitted particles are parallel this is called the Gamow-Teller decay (Gamow and Teller, 1936); when antiparallel, it is known as the Fermi decay. Thus measurement of parity/spin of $0^+ \rightarrow 0^+$ allows for only a Fermi transition, as this angular momentum cannot be accomplished via Gamow-Teller decay. (Rubio and Gelletly, 2009). In cases where both types of decay selection rules are met, mixed Fermi/Gamow-Teller transitions can occur. Due to the charge independent strong force, neutrons and protons can be thought of particles with distinctly similar properties, leading to the nucleons being defined by their isospin, whereby their states can change. However by using the Gamow-Teller and Fermi transitions, one can determine the neutron and proton transition probabilities.

2.7.2.5 Allowed and forbidden $\beta$ transitions

$\beta$ decay transitions can be classed as forbidden or allowed, depending on the angular momentum and parity selection rules outlined above, between the initial and final states of the decay. Defining decays as completely forbidden is not correct. ‘Forbidden’ transitions do take place; however the probability of their decay is much less than those that are ‘allowed’ to decay and they also have much longer half-lives. When selection rules for allowed decay are compromised, forbidden decays can occur when the initial and final states have opposite parities (Krane, 1998). Thus in $\beta$ decay the higher the order of a forbidden transition, the less
likely it is for the decay to occur. The conditions for the allowed and the first few forbidden transitions can be found in Table 2.1.

| Transition Type          | Relative orbital angular momentum (L) | Fermi $|I_i - I_f|$ | Gamow-Teller |
|-------------------------|---------------------------------------|------------------|----------------|
|                         |                                       | $\Delta I$       | $\Delta \pi$   |
| Allowed                 | 0                                     | 0                | No             |
| First-forbidden         | 1                                     | (0), 1           | Yes            |
| Second-forbidden        | 2                                     | (1), 2           | No             |
| Third-forbidden         | 3                                     | (2), 3           | Yes            |
| Fourth-forbidden        | 4                                     | (3), 4           | No             |

Table 2.1 - $\beta$ decay allowed and forbidden selection rules; table taken from (Krane, 1998).

2.7.3 Gamma decay and Internal Electron Conversion

Following $\alpha$ or $\beta$ decay the spin and parity selection rules means that it is possible that the daughter nuclide can be populated in an excited state, which itself de-excites to a lower energy excited state or the ground state by the emission of a photon of electromagnetic radiation ($\gamma$ ray). The $\gamma$-ray energy is equal to that of the energy difference between the nuclear states (ignoring the negligible recoil energy of the emitting nucleus). When this de-excitation proceeds to an intermediate energy state a cascade of $\gamma$ rays is possible, until the ground state is reached. Gamma rays have energies typically in the range of 0.1 to 10 MeV. The available nuclear mass energy does not always give rise to the emission of a $\gamma$ ray. The nuclear electromagnetic field may instead interact directly with an orbital atomic electron, resulting in its ejection from the atom with fixed energy equal to the excitation energy minus the binding energy of the shell from which it was ejected. This competing process is known as internal conversion and the ejected electrons are known as conversion electrons. Since the electron
binding energies vary with atomic orbital, for a given gamma transition, conversion electrons may be ejected at various discrete energies.

2.7.3.1 Angular Momentum and Parity Selection Rules in Electromagnetic Transitions

The selection rules for angular momentum and parity selection for a $\gamma$ transition from an initial state of spin/parity $I_i^\pi$ to a final spin/parity $I_f^\pi$ which can be defined by the basic conservation laws, as to produce a photon whereby the integer $L$ determines the multipole order, such that:

$$|I_i - I_f| \leq L \leq I_i - I_f \quad (no \ L = 0) \quad (Equation \ 2.31)$$

while the parity ($\pi$) change of the transition is given by the following selection rules for Electric ($E$) and Magnetic ($M$) transitions:

$$\Delta \pi \ (EL) = (-1)^L$$

$$\Delta \pi \ (ML) = (-1)^{L+1}$$

Photons have an intrinsic spin of $1\hbar$, and therefore direct transitions between two $0^+$ or $0^-$ (where $\Delta L = 0$) are strictly forbidden. These transitions occur instead via internal pair formation or internal conversion.

2.7.3.2 Internal conversion

Unlike $\beta$ decay the electrons are present previously in the atomic orbit and not created in the decay process. Internal conversion is not a two-step process (Kibédi, et al, 2008) thus $\Delta E$ can be defined as the kinetic energy $T_e$. Internal conversion can thus be defined as:
\[ E_e = E_\gamma - BE_e \quad (Equation \ 2.32) \]

where \( E_\gamma \) is the energy of the competing \( \gamma \) ray. The term \( BE_e \) is the atomic binding energy of the emitted electron. As in the case of electron capture decay, the resulting vacancy in an inner electron shell results in a cascade of atomic electrons and the emission of the spectrum of characteristic X-rays of the daughter element, along with any associated Auger electrons. The ratio of the probabilities for conversion electron emission to \( \gamma \) ray emission for a particular transition is known as the internal conversion coefficient \( (\alpha) \) and is given by:

\[ \alpha = \frac{\lambda_e}{\lambda_\gamma} \quad (Equation \ 2.33) \]

which can be re-written as:

\[ \lambda_{TOT} = \lambda_\gamma (1 + \alpha) = \lambda_\gamma + \lambda_e \quad (Equation \ 2.34) \]

where \( \lambda_{TOT} = \) total decay rate \( \lambda_e + \lambda_\gamma \) and \( \lambda_\gamma \) is the \( \gamma \)-ray emission probability. The term for \( \alpha \) can be sub-divided depending on the individual \( K \) and/or \( L \) shells where the electrons are considered. In general, the process decreases with increasing \( \gamma \) ray energy, and is usually negligible for high energies (Kibédi, et al, 2008, BrIcc conversion calculator).

Although most \( \gamma \) transitions occur in prompt succession to the original decay mode feeding the excited state, (usually within at most, nanoseconds), some states may exist for longer periods.
The transitions from such isomeric or metastable states (indicated with a superscript m, i.e.: $^{99m}$Tc) are known as isomeric transitions (Dracoulis, et al, 2013) as they involve nuclear decay to the same nuclide.

2.7.4 Nuclear reactions

If $R$ is the rate of a certain group of radionuclides that are produced in a nuclear reaction in some time period $\Delta t$, then the total number of nuclides of this type present will be determined by the number created by the reaction, minus the number that radioactively decay in the same time period. This will depend on the number of target atoms $N_0$, on the reaction cross section $\sigma$ and on the flux or current $I$ of incident particles (Choppin, et al, 1998). Such that,

$$R = N_0 \sigma I \quad (Equation \ 2.35)$$

If one denotes the number of radioactive nuclei that are formed by the reaction as $N_I$ and that these nuclei decay with a decay probability $\lambda_I$, to a number of stable nuclei denoted by $N_2$. Here an example of a one-step product and decay $N_I$ increases owning to the production at the rate $R$ and decreases owning to the radioactive decay:

$$dN_I = R \ dt - \lambda_I N_I dt \quad (Equation \ 2.36)$$

$$\therefore \ N_I(t) = \frac{R}{\lambda_I} (1 - e^{-\lambda_I t})$$
2.7.4.1 Conservation laws and energetics

Nuclear reactions can be written schematically:

\[ X (a,b) Y \]  \hspace{1cm} (Equation 2.37)

where \( X \) is the target nuclear species, \( a \) is the accelerated projectile, \( b \) is the ejectile and \( Y \) is the residual (heavy) nucleus formed via the reaction. Of the reaction projects, \( b \) is usually a light particle that can sometimes be detected directly following the reaction, while \( Y \) is the heavy product which usually stops in a thick production target and is not directly observed (Krane, 1998).

An important reaction carried out in this thesis, can be written as,

\[ ^{238}\text{U}(p,3n)^{236}\text{Np} \]  \hspace{1cm} (Equation 2.38)

Here the neutrons are not really ‘ejectiles’ but rather sequentially evaporated neutrons.

The conservation laws and energetics of nuclear reactions are analogous with those applied in radioactive decay. Through the laws of the conservation of total mass energy and linear momentum, the measured energy of \( b \) to determine the excitation energy of states of \( Y \) or mass difference been \( X \) and \( Y \), i.e. the difference in mass between the \( ^{238}\text{U} \) and the \( ^{236}\text{Np} \) in the reaction outlined in Equation 2.38. The population of discrete angular momentum states can be deduced through applying the laws of conservation of angular momentum, thus conservation of parity also exists. However, it must be noted that these laws are different for:
1. Direct transfer reactions (e.g. (d, n)) and
2. Fusion evaporation reactions (e.g. $^{238}$U(p,3n))

### 2.7.4.2 Production rates and reaction cross sections

The rate of radionuclide production depends on a variety of factors, including the incident particle energy, the thickness of the target in terms of “target” nuclei per unit area (cm$^2$), the magnitude of the reaction cross-section as a function of energy and the flux or beam current of incoming particles.

The rate of production is given by (IAEA, 2011):

$$-\frac{dn}{dt} = R = nI(1 - e^{-\lambda t}) \int_{E_s}^{E_0} \frac{s(E)}{dE/dx} dE \ (Equation \ 2.39)$$

Where:

- $R$ is the number of nuclei formed per second
- $n$ is the target thickness in mg/cm$^2$
- $I$ is the incident particle flux per second and is related to the beam current
- $\lambda$ is the decay constant and is equal to $(\ln 2)\times T_{1/2}$
- $t$ is the irradiation time in seconds
- $s$ is the reaction cross-section expressed in cm$^2$ (1 barn = $10^{-24}$ = $10^{-28}$ m$^2$)
- $E$ is the energy of the incident particles (i.e. = beam energy)
- $x$ is the distance travelled by the particle (i.e. the thickness of the target with the incoming particle travels before interacting and where the reaction occurs.)
- $\int_{E_s}^{E_0}$ is the integral from the initial to the final energy of the incident particle along its path (i.e. takes into account any loss/reduction in beam energy along the finite target thickness.)
Reaction cross sections measure the probability of a beam particle interacting with the target nucleus. The reaction cross section is given by:

\[ \sigma = \frac{R_b}{I_a} \]  

(Equation 2.40)

where \( \sigma \) is usually given in terms of barns where 1 barn = \( 10^{-28} \) m\(^2\) = \( 10^{-24} \) cm\(^2\).

In the equation \( R_b \) is the number of reactions per unit time per nucleus, \( I_a \) is the current of incident particles per unit time (Krane, 1998).

### 2.7.4.3 Fusion evaporation reactions

The favoured production routes used in this current thesis for \(^{236}\text{g} \text{Np}\) were fusion-evaporation reactions, specifically \(^{238}\text{U}(p,3n)^{236}\text{Np}\). Fission induced by light particle interactions such as with a beam of protons are of interest due to the small angular momentum transferred to the compound system and the ability to reach excitation energies of the compound system which mirror fast neutron induced reactions. Most of the beam particles in these reactions miss the target nuclei, due to the \( \sim 10^{-14} \) m scale of the nucleus. Consequently, the cross section for fusion drops for heavier nuclei, where induced fission begins to take over from fusion-evaporation reactions. Fusion-evaporation reactions are a method to produce excited nuclei with relatively high spin states and require the formation of a compound nucleus. The reaction allows for two stable nuclei at collision energies above the Coulomb barrier to be brought together, where the kinetic energy of the collision in the centre mass frame is converted into excitation energy of the compound system. The system is one that lives long enough (> \( 10^{20} \) s) (Egidy, 1988) for thermodynamic equilibrium to occur, during which time the compound system ‘loses its memory’ of how it was formed in terms of the make-up of the target and projectile nuclei. Significantly the higher energy of the beam particles in the reaction, the more angular
momentum is transferred into the compound system. This compound system consequently evaporates nucleons and then decay by γ-ray emission, typically producing residual nuclei on the neutron-deficient side of the valley of stability. Fusion reactions only occur for small values for impact parameter, while other reactions take place at increased target-beam distances such as Coulomb excitation.

2.7.4.4 Nuclear fission

When bombarding a natU target with protons a variety of other radionuclides including primary fission products are produced. Neutron-induced fission was initially discovered by Otto Hahn and Fritz Strassman (Hahn and Strassman, 1939) by bombarding uranium with neutrons, forming a series of intermediate-mass nuclei and a large (compared atomic processes) release of energy (~ 200 MeV).

The fission fragments produced are expected to range in mass (typically from $A \sim 70$), where the combined number of nucleons ($A$) cannot exceed the initial number (Hodgson, 1997). However, each fission reaction is unique and different mass partitions of fission fragment mass distributions are possible.
Figure 2.8- Fission yields for neutron induced and spontaneous fission for common nuclear fuels (Kellett, et al, 2009).

The mass distribution is affected by the stability of the fission fragments, and produces a double-peaked distribution (Figure 2.8). Where the population of fission fragments related to their proximity to nuclear shell closures show a common maximum at $A = 95$ and $A = 140$ for the particle induced fission of $^{238}$U (Kellett, et al, 2007). The mass distribution changes with increasing incident neutron or proton energy with a relative increase in the symmetric fission components (Kellett, et al, 2007). Fission fragment residues isotopes between $A \sim 70$ and $A \sim 170$ mass region are neutron rich in nature and to reach stability undergo $\beta$ decay towards nuclear stability. These decays will continue until a stable isobar is reached, i.e. the end of their respective decay chain.
2.7.4.5 Nuclear Decay Data

All decay data values obtained and used in this thesis were taken from a number of different databases. The Evaluated Nuclear Structure Data file (ENSDF) was used for all fundamental nuclear structure information and level schemes. The JEFF (Joint Evaluated Fission and Fusion file) data library, which is part of the Nuclear Energy Agency (NEA) data bank member countries, was used for nuclear decay data, due to ease of its use and accessibility. In addition to JEFF the National Nuclear Data Centre (NNDC), which is part of the Brookhaven National Laboratory, was used as an additional quality assurance check and comparison to ensure the most up to date data was being used for the work.
Chapter 3

3. Radiochemistry Overview for Actinide Chemistry

3.1 Chemical separation and sample dissolution

Radiochemical separation becomes necessary when it is not possible to determine the activity of a radionuclide by direct measurement. The rigour of a radiochemical clean-up is defined by the data quality objectives set for the measurement, which in turn depend on the detection method (Jerome, et al, 2012). Selection of a particular measurement technique will place further limitations on the type of active source that is presented to the detector. Non-destructive analysis of radionuclides is only usually possible for photon emitting radionuclides that can be measured directly by high resolution γ-ray spectrometry. In many cases, particularly for heavy elements, γ-ray spectrometry may not be possible or may not deliver the required sensitivity. So, it becomes necessary to isolate and concentrate the nuclide of interest from the sample matrix.

Although α particles are emitted with a discrete and characteristic energy, α particles emitted by different radionuclides may not be capable of being resolved with commonly used equipment. Therefore, with both α-spectrometry and ICP-MS measurements it is critical that the spectra show clear separation between thorium in the uranium spectra and vice versa (Maxwell, et al, 2015). This is of importance for NORM measurements using α-spectrometry where the $4n$ Thorium series and $4n + 2$ Uranium series dominate, where interfering alphas in a measurement make it difficult to identify and quantify the various isotopes in the spectra. This is due to peak overlap as a result of improper radiochemical separation, this inevitability degrades the alpha peak shape and limits achievable resolution (Horwitz, et al, 1992). According to Casacuberta, et al, (2012) and Horwitz, et al, (1997) classical methods used for
uranium and thorium separation are liquid–liquid extraction, solid phase extraction and anion exchange chromatography (Bolivar, 1995). According to Horwitz, et al (1997) it is essential analytical grade or traceable grade reagents are used to ensure no contribution to method background levels from Naturally Occurring Radioactive Materials is present. This has been proven and validated from previous tests on other projects (Harms and Gilligan, 2012) of reagents and by using traceable agents that are certificated to prevent any interference with the analysis in the project.

3.1.1 Sample dissolution

A recent proficiency test exercise carried out by the U.S Department of Energy Mixed Analyte Performance Evaluation Program (MAPEP), indicated that approximately 80% of participating laboratories failed to accurately determine uranium isotopes in soil samples, due to incomplete dissolution of refractory particles in the samples (Maxwell, et al, 2011b).

The NORM reference materials are solid complex mineral matrices. In order to work with these systems and to isolate radionuclides of interest, silicates need to be adequately dissolved in order to assure dissolution of the radionuclides incorporated inside the silicate crystal structure of soils (such as natural uranium/thorium). It is also necessary to eliminate it from the matrix before starting the radiochemical analysis, as silica-monomers may transform into insoluble polymeric colloids or even precipitate (Grinberg, et al, 2007).

The main techniques for sample decomposition are fusion, wet ashing and microwave digestion (Croudace, et al, 1998). Dissolution using HNO₃ or HCl has frequently been applied, and for sample destruction a mixture of acids including hydrofluoric and perchloric acids, and hydrogen peroxide have been effectively used, in some cases using high pressure microwave digestion (Grinberg, et al, 2007; Taylor, et al, 2007; Feuerstein, et al, 2008; Amr and Abdel-
Lateef, 2010; Vajda and Kim, 2010; Amr, 2016; Wang, 2004). However, these techniques have shown incomplete digestion of samples and variable chemical recoveries due to interference from major salt ions leading to the so-called ‘matrix effects’ (Lee, et al, 2001). In addition, the use of hydrofluoric acid is problematic due to it being (extremely) toxic and because excess fluoride ions from hydrofluoric acid can cause problems with separation procedures as it is such a strong complexing agent (Horwitz, et al, 2005). Fusion methods have been reported by Croudace, et al, (1998); Vajda, et al, (2009) and Reading, et al, (2015) where actinides were fused by borate fusion methods, which showed both high recoveries and ensured that the refractory particles were suitably digested, it is known to be effective in dissolving minerals and rocks comprising oxides, carbonates, chlorides, sulphates, and phosphates (Reading, et al, 2015). Borate fusion using the 2015 5-station Katanax K2 electrical fuser (Katanax, Canada) is the technique of choice for the digestion of the NORM reference materials in order to carry out chemical separation for the direct measurement of thorium and uranium.

Some elements show issues with volatility with fusion (Bock, 1979; Parsa, 1992). A key factor in the preparation and analysis of samples for $^{210}\text{Po}$ is the caution required to avoid losses due to volatilisation (Mathews, 2007). Thus, the sample preparation procedure did not use the Katanax method outlined above as fusion techniques from various studies showed substantial losses of polonium (Akbar, Hutton, & Prescott, 1985; Lowson & Short, 1986). Even with dry ashing, loss of polonium may occur at temperatures as low as 100 °C, with virtually all polonium lost as the temperature approaches 800 °C (Cleary and Hamilton, 1968). Clearly, temperatures should be kept as low as the chosen procedure permits, however it has also been found that HNO$_3$ digestion alone has shown incomplete $^{210}\text{Po}$ extraction (Card and Bell, 2005). The procedure followed in this work was as used by Vreček, et al, (2004) where samples were digested in Teflon beakers under prolonged acid leaching, rather than total dissolution.
3.1.2 Radiochemical separation techniques

The following section outlines the different forms of chemical separation techniques that were used in the current work.

3.1.2.1 Principles and uses of Ion Exchange Resins

The principle of ion-exchange chromatography is based on synthetic resins that have ion exchange properties (Adams and Holmes, 1935). The method is centred on the principle that molecules within the medium are separated according to their respective charge (Faris, 1964) where there is a reversible exchange of metal ions between the resin, which acts as a solid ionic phase, and a liquid phase of opposite charge which is typically aqueous (Korkisch, 1989). The solid phase in this work is a permeable but insoluble polymer based on styrene divinylbenzene, that may bind with mobile counter-ions of opposite charge that compete with the ion-solvent interactions in the liquid phase, causing selective partition of ions. Thus when a sample is passed through the column the molecules that are neutral or bear the same charge as the functional groups are eluted, while oppositely charged molecules compete with the counter ions for binding sites on the functional groups (Horwitz, et al, 1991). Molecules that are more highly charged than the counter ions are bound to the matrix and are retained in the column. An eluent with the appropriate ionic strength and pH can then be used to recover the bound sample, allowing for separation of different elements (Korkisch, 1989).

To determine the efficiency of separation in ion-exchange systems, both the separation factor, $a$ and the weight distribution coefficient $K_d$, which can be defined as:

$$K_d = \frac{[C_1/g_{resin}]}{[C_2/m_{solution}]} \quad (Equation \ 3.1)$$
In this expression $C_1$ is the mass of metal ion absorbed on a gram of dry resin, whereas $C_2$ is the mass of metal that remains in solution once equilibrium has been reached. The ratio of the distribution coefficients is used to define the separation factor, ($\alpha$), where:

$$\alpha = \frac{K_{d,a}}{K_{d,b}} \quad (Equation \ 3.2)$$

$a$ and $b$ refer to a respective pair of ions. This ratio determines the degree of separation between the two ions where separation will only be achieved if $\alpha \neq 1$. The more that $\alpha$ differs from unity, the easier it will be to obtain separation. A significant process in ion-exchange chromatography is diffusion, in order for the ion exchange process to take place.

![Figure 3.1 - Scanning Electron Microscope image of AG1 ion-exchange resin used in the current work.](image)

According to Korkisch, (1989) equilibrium is established between each ion in the analyte solution and the exchange site on the resin. The resin used in this investigation was the Bio-Rad Analytical grade 1-X8 100-200 mesh (analytical grade anion resin 8% cross linking, 75
-150 µm particle diameter), which is a strongly basic anion resin comprising of polystyrene cross-linked with divinylbenzene. The cross link between the polymers is determined by the amount of the divinylbenzene used. The 8% cross linking means that the pore size of polystyrene and polyacrylic acid resins use effectively limits their use to molecules weighing less than 500 (Korkisch, 1989). Large molecules cannot penetrate these resins and that the flow rate of an ion-exchange resin is primarily determined by the particle size of the resin.

Bunney, et al (1953) demonstrated that adsorption of uranium and thorium on an anion exchange resin depends on the strength of the hydrochloric acid used, as the pH strength of the hydrochloric acid is used so is the adsorption of uranium. Authors such as Lally et al (1978) and Korkisch (1961) have used both a combination of nitric and hydrochloric acid to carry out the chemical separation of thorium and uranium.

3.1.2.2 Principles and uses of Solvent Extraction

Solvent extraction is a traditional technique that is widely adopted in many analytical laboratories around the world. Although not as widely used as they once were, due to costs of disposing of organic waste, the environmental impact of using volatile solvents and the time and labour intensive processes adopted in the technique is still of significance, especially in analytical procedures where uranium extraction is necessary (Tan, et al, 2015).

The technique is based on the principle using a solvent to partition the solute from a liquid based mixture. It is a process whereby a solute is shaken with an organic solvent containing organic extractants. Once the phases have separated, the ratio of the concentration of solute 

\( K_d \) in the two phases will be a constant, however it must be said that the process although
selectively dissolves the solute in one solvent does not remove the solute completely from the other solvent. The process can be shown as:

\[
K_d = \frac{[C_1]_{organic}}{[C_2]_{aqueous}} = \frac{[S_{org}]}{[S_{aq}]} \quad (Equation \ 3.3)
\]

\(K_d\) is the distribution coefficient which is an equilibrium constant that describes the difference in solubility of a particular solute in the solvent pairs of an extraction system and is the main parameter which characterises the extraction process. The coefficient must be used as an approximation and is not thermodynamically rigorous. It does not take into account in complexes where the solute is involved in the chemical reaction, such as in association and dissociation reactions.

The terms \(S_{org}\) and \(S_{aq}\) are the concentration of solute in the organic solvent and in the aqueous phase respectively (g/cm). The extractant removes the analyte from aqueous phase whilst leaving interfering ions. It does this through the formation of an analyte extractant complex which is more soluble in the organic phase. The purified analyte can then be extracted back from the organic phase into a separate aqueous phase by adjustment of the extraction conditions (Longworth, 1998).

### 3.1.2.3 Solvent extraction to remove uranium

Solvent extraction can be used to isolate either single actinides or to pre-concentrate actinides (Laskorin, et al, 1985). Solvent extraction has been used to remove uranium from solution since the nineteenth century when Peligot (1842) used diethyl ether to remove the actinide from nitric acid solutions (Stary, 1964). From the later 1940s up until the later part of the twentieth century,
plutonium production for the development of nuclear weapons was the principal driver for the development of the chemical separation of actinides. Chemicals such as methyl isobutyl ketone (MIK) have been used to extract uranium from nitrate solutions, and specifically used in the nuclear industry to chemically separate uranium and plutonium from spent fuels in the REDOX process (Taylor, et al, 1997). Warf (1949) showed that tri-n-butyl phosphate (TBP) can extract U in the form of $\text{UO}_2(\text{NO}_3)_2 \cdot 2(\text{C}_9\text{H}_9\text{O})_3\text{PO}$ from nitric media due to its high distribution coefficient. There is much literature discussing uranium recovery from the TBP complex as the process is widely used in the nuclear industry in the PUREX process (Taylor, et al, 1997).

3.1.3 Principles and uses of Extraction Chromatography

Extraction Chromatography which was proposed by Siekierski in 1959 as a potential method in separating metal ions. The technique involves resins that are made up of extractant materials that are absorbed onto an inert polymeric support matrix (Figure 3.2).

Figure 3.2- Schematic view of a typical extraction chromatography resin (Triskem website).
The technique has been developed in recent years (Horwitz, et al, 1997) since it combines the benefits of the simple operation of ion-exchange column chromatography but with the selectivity of liquid-liquid extraction. The technique has the added advantage of reducing the volume of the organic and acidic solutions used in the analysis and thus reducing the separation time and attributed cost involved (Lehritani, et al, 2012). The extraction chromatographic system can be portioned into three components (Horwitz, et al, 1997); inert support phase which is made up of an organic polymer, a stationary phase that is typically a liquid extractant and the mobile phase which is, in most cases, either hydrochloric or nitric acid solution. According to EICHROM in order to achieve chemical separation using the extraction chromatography resins, band spreading must be sufficiently small to avoid early breakthrough and to avoid excessive cross-contamination of the constituents that one is trying to separate.

The corresponding system is given as:

\[ k' = \frac{D V_S}{V_m} \]  

(Equation 3.4)

In this expression \( k' \) is the number of free column volumes of eluent required to reach peak maximum, which like the distribution ratio, is not measured directly by the extraction chromatography system but calculated from the weight distribution ratio \( D_w \). \( V_S \) and \( V_m \) are the volume stationary and mobile phases respectively. The weight distribution ratio, \( D_w \), is given by the following expression:

\[ D_w = \frac{A_0 - A_s}{A_s} \left( \frac{mL}{g} \right) \]  

(Equation 3.5)
It is derived by the amount of a given metal ion taken up by a measured weight of resin from a given volume of aqueous solution (Horwitz, et al, 1997). The term \( A_0 - A_s \) is the activity of material that is sorbed on a given weight of resin, while \( A_s \) and \( g \) is the activity in a known volume, mL of solution. Thus the volume distribution ratio \( D \) is calculated from the volume of stationary phase per gram divided into \( D_w \).

### 3.1.3.1 EICHROM resins

The extraction resins selected for this work are based on the methods applied at EICHROM Technologies, Inc., Darien, IL (Dietz and Horwitz, 1993; Horwitz, et al, 1991, 1992a, and 1993). The resins are based on materials that are based on technologies such as crown ethers and inorganic absorbers that allow for effective chemical separation. The separation is achieved by ensuring a small band spreading to ensure that cross-contamination does not occur between the various constituents of a sample that are to be separated. The resins also cover a wide range of selectivity, this is of significance due to the range of nuclides under investigation in this work. EICHROM resins can be used to separate a wide range of selectivity’s whether NORM nuclides, neptunium and fission products (Horwitz, et al, 1991). Each resin has an extractant which is designed to be used in the separation of a particular metal ion from a complicated matrix of nuclear materials.
The following resins will be used in this work:

<table>
<thead>
<tr>
<th>Material</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRU resin</td>
<td>Actinides(III, IV, VI), Ln(III)</td>
</tr>
<tr>
<td>TEVA resin</td>
<td>Th(IV), Np(IV), Pu(IV), Tc(VII))</td>
</tr>
<tr>
<td>UTEVA resin</td>
<td>U(VI) and tetravalent actinides</td>
</tr>
<tr>
<td>Sr Resin</td>
<td>Sr</td>
</tr>
</tbody>
</table>

Table 3.1- EICHROM resins used in this EngD thesis.

### 3.1.3.2 TRU resin

TRU resins are used in the extraction and chemical separation of transuranics. The stationary phase of the resin consists of 0.75 M octyl(phenyl)-N,N-di-isobutyl carbamoyl methylphosphine oxide (CMPO) in tributyl phosphate (TBP) coated onto an inert polymeric support. The combination of the TBP and the CMPO allows for the increase in update of trivalent actinides such as Am(III) and other tetra and hexavalent actinides (Horwitz, 1995). Various authors have used TRU resins for the separation of actinides in urine and soil samples (Maxwell, 2008b) prior to analysis using ICP-MS.
Figure 3.3- Acid dependencies of HCl for the uptake of several Actinides by TRU (figure taken from EICHROM Industries Inc, 2005).
3.1.3.3 TEVA resin

TEVA resin contains a trialkylmethylammonium nitrate as the stationary phase and is used predominantly for the separation of tetravalent actinides (Horwitz, 1995). Its attributes are similar to those discussed in anion exchange resins, as it is possible to sorb the tetravalent actinides at range of nitric acid concentrations. The reason the TEVA resin is used in place of the anion exchange resin is due to its chemical makeup, with it having a liquid form rather than a polymer backbone. This means that greater mobility exists in order to coordinate around target anions, thus leading to an increased uptake of ions in actinide elutions often at lower acidic concentrations.

TEVA resin is used predominately for the separation of tetravalent Np, Pu and Th (Horwitz, 1997). Np and Pu are sorbed from a wide range of hydrochloric and nitric acid concentrations (Figure 3.4), whereas Th is retained by nitric acid. Horwitz determined that the advantages of using TEVA can be that both Pu and Np can be separated by 3 M nitric acid, and significantly the thorium separation is not subject to tailing, with uranium elution requiring less nitric acid solution. In addition, TEVA columns can be used in a stacked column approach with either UTEVA and TRU columns for the separation of actinides.
Figure 3.4- Acid dependencies of HCl and HNO$_3$ for the uptake of several Actinides by TEVA (figure taken from EICHROM Industries Inc, 2005).

The resin is also of potential interest in this work for the NORM analysis of reference materials as many of the cations that often interfere with measurements are not retained by the resin, thus allowing for the isolation of Th from other elements in the $\alpha$-spectrometry/mass spectrometry analysis of the $4n$ Thorium decay series that was carried out in this work.
3.1.3.4 UTEVA resin

UTEVA resins contain diamyl amylphosphonate (DAAP) as the stationary phase (Horwitz, 1997) where the resin extracts U(VI) as a neutral nitrate complex. The resin is commonly used in environmental analysis to measure uranium and thorium. Due to the large difference in $k'$ for uranium and thorium in the range of 4-6 M HCl, U and Th can be selectively eluted from NORM samples where U is typically eluted using dilute acid (Figure 3.5). The benefit of the technique is that many cations such as Fe, Na, Ca, which can typically interfere in measurements, are not retained by the resin, thus the resin is especially useful for measurement of U and Th in the NORM samples analysed in this current work (Chapter 5). As the uranium/neptunium and uranium/thorium separation factors are better in hydrochloric acid, elution sequences involving a cross over from nitric to hydrochloric acid may offer a means to isolate and sequentially elute several actinides in a single run. This is the basis of the method described by EICHROM for the separation of thorium and uranium in NORM materials. Casacuberta, et al, 2012 discussed an optimum radiochemical separation method by extraction chromatography using UTEVA resins for solid and liquid samples with enhanced concentrations of both uranium and thorium isotopes and obtained a method to quantify U and Th in NORM samples (Pilvio and Bickel, 2000).
Figure 3.5 - Acid dependencies of HNO₃ for the uptake of several Actinides by UTEVA and TRU (EICHROM Industries Inc, 2005).

In addition, this method has been used by Taylor, et al, (2007) to isolate uranium for measurement using Thermal Ionization Mass-Spectrometry (TIMS). Croudace, et al, (1998) developed a rapid procedure for plutonium and uranium determination in soil using anion-exchange and UTEVA resin. The plutonium and thorium are isolated on an anion-exchange column prior to passing the uranium fraction through the UTEVA column.
3.1.3.5 Sr resin

Extraction chromatography using commercially available Sr-resin (Triskem International) is a rapid and straightforward technique, which has been extensively applied to separation of $^{90}$Sr from both radiometric and mass spectrometric interferences in a range of sample matrices including water, plants and sediments (Vonderheide, et al, 2004; Isnard, et al, 2006; Grinberg, et al, 2007; Taylor, et al, 2007; Feuerstein, et al, 2008). The material consists of an extractant (4,4′(5′)-bis(t-butylcyclohexano)-18-crown-6) (Figure 3.6) diluted in octanol solution and sorbed on an inert polymeric support (Vajda and Kim, 2010).

$$\text{Sr}^{2+}_{\text{aq}} + \text{Crown}_{\text{org}} + 2\text{NO}_3^{-}_{\text{aq}} \rightleftharpoons \text{Sr(Crown)(NO}_3)_2\text{org} \quad (Equation\ 3.6)$$

![Figure 3.6- The extractant system in Sr-resin: (4,4′(5′)-bis(t-butylcyclohexano)-18-crown-6).](image)

In addition to Sr, the resin has proven to be a suitable method in separating Po as, in order to achieve low detection limits, chemical separation of Po is required. The maximum distribution coefficient for Po on Sr resin is about $10^2$ in nitric acid, which is approximately between 0.5-1 mol l$^{-1}$, decreasing at higher levels (Horwitz, et al, 1992). In the method developed by Vajda, et al, (2007), recoveries estimated to be approximately 70% are reported (Vajda, et al, 1997).
Po is usually loaded onto the solid phase from > 2 M HCl solution and stripped with 6 M HNO₃ (Vajda, et al, 1997; Miura, et al, 2000; Biggin, et al, 2002).

3.2 Literature review of actinide chemistry

3.2.1 Oxidation and Reduction processes of the actinide series

The difference in mass number of all isotopes of the same element are generally small enough that they essentially exhibit the same chemical behaviour. Thus a stable source of Pb exhibits similar chemical characteristics to the radioactive isotope ²¹⁰Pb. However, and especially so for uranium, neptunium and plutonium, where several different oxidation states of these elements may coexist in solution, good redox control is critical in ensuring consistent chemical behaviour is achieved. With the presence of oxygen, water, acids or other potential oxidants and reductants that may be in carrier solutions, the oxidation state of the radionuclide may change based on either natural or induced redox processes. Thus, the oxidation state is the indication of the formal charge on the ion. For instance Th(IV) implies that Th⁴⁺ is present, but this may be in solution as (for example) [Th(H₂O)₆]⁴⁺ or [Th(NO₃)₆]²⁻, which behave differently.

3.2.2 Actinide properties

The oxidation number of actinides is discussed in detail by Cotton and Wilkinson (1988). The actinide series exhibit a range of oxidation states, thus making redox control challenging, the hydrolytic behaviour of the ions and the chemical behaviour of the actinides, makes the series one of the most complex chemically in the periodic table. The actinides are a group of 15 chemical elements from Actinium (Z = 89) to Lawrencium (Z = 103) which sharing analogous properties to the 15 lanthanide elements. They are all metals with large atomic radii and exist in chemical compounds and in solution as cations with very large ionic radii. The actinide
series have a unique feature whereby the outermost electronic subshell has a unique transition series, and thus their chemical properties are governed by the features of the outermost electronic subshell. As the atomic number increases from 90, electrons are added in the 5f subshell (Table 3.2). The series would then be expected to terminate at element 103 (Lr) as this would lead to 14 electrons being added to the shell, thus leading to a completed 5f subshell. The series has a large range of oxidation states in metallic metals. In the elements that are lighter than Pu (Z = 94) the 5f orbitals are sufficiently diffuse that the electrons in these orbitals are itinerant (delocalized, chemically bonding, often with unique magnetic moments and electrical conductivity, whereas heavier than plutonium these electrons are localised and do not contribute significantly to conductivity or chemical bonds. The various energy levels of the 5f, 6d and 7s electrons have a close proximity, thus leading to multiple oxidation states for the ions that are found in the lighter actinides (Table 3.2).

The actinides of significant interest in this work, are Np (production of $^{236}$Np), U and Th (measurement of NORM reference materials). The following sections will provide further details on their radiochemistry and radiochemical separation methods used to isolate and subsequently quantify the activities of the various materials to be measured in this work.
<table>
<thead>
<tr>
<th>Atomic number</th>
<th>Element</th>
<th>Atomic configuration</th>
<th>Oxidation states*</th>
</tr>
</thead>
<tbody>
<tr>
<td>89</td>
<td>Ac</td>
<td>5f⁰6d⁷s²</td>
<td>3</td>
</tr>
<tr>
<td>90</td>
<td>Th</td>
<td>5f⁰6d⁷s²</td>
<td>(3) 4</td>
</tr>
<tr>
<td>91</td>
<td>Pa</td>
<td>5f⁰6d⁷s²</td>
<td>(3) 4 5</td>
</tr>
<tr>
<td>92</td>
<td>U</td>
<td>5f⁰6d⁷s²</td>
<td>3 4 5 6</td>
</tr>
<tr>
<td>93</td>
<td>Np</td>
<td>5f⁰6d⁷s²</td>
<td>3 4 5 6 (7)</td>
</tr>
<tr>
<td>94</td>
<td>Pu</td>
<td>5f⁰7s²</td>
<td>3 4 5 6 (7)</td>
</tr>
<tr>
<td>95</td>
<td>Am</td>
<td>5f⁰⁷s²</td>
<td>3 4 5 6</td>
</tr>
<tr>
<td>96</td>
<td>Cm</td>
<td>5f⁰6d⁷s²</td>
<td>3 4</td>
</tr>
<tr>
<td>97</td>
<td>Bk</td>
<td>5f⁰⁷s²</td>
<td>3 4</td>
</tr>
<tr>
<td>98</td>
<td>Cf</td>
<td>5f¹⁰⁷s²</td>
<td>(2) 3</td>
</tr>
<tr>
<td>99</td>
<td>Es</td>
<td>5f¹¹⁷s²</td>
<td>(2) 3</td>
</tr>
<tr>
<td>100</td>
<td>Fm</td>
<td>5f¹²⁷s²</td>
<td>(2) 3</td>
</tr>
<tr>
<td>101</td>
<td>Md</td>
<td>(5f¹³⁷s²)</td>
<td>2 3</td>
</tr>
<tr>
<td>102</td>
<td>No</td>
<td>(5f¹⁴⁷s²)</td>
<td>2 3</td>
</tr>
<tr>
<td>103</td>
<td>Lr</td>
<td>(5f¹⁴⁶d⁷s²)</td>
<td>3</td>
</tr>
</tbody>
</table>

*Indicates the most stable oxidation state, the oxidation state stated in parenthesis is the most unstable or one found in the solid state.

Table 3.2- Electronic configuration and oxidation states of actinides.
3.2.3 Uranium chemistry in aqueous solution

Understanding U chemistry is significant both in the irradiation of uranium targets for the production of $^{236}$Np, but also for the measurement of NORM in the reference material characterisation part of the work.

Uranium is most stable in aqueous solution in the $6^+$ oxidation state where the linear uranyl(VI) ion, $\text{UO}_2^{2+}$, as the stable entity (Grenthe, 2004). It is well known that uranium, as the uranyl cation $\text{UO}_2^{2+}$, is highly soluble in a number of oxygen containing organic compounds. This has been exploited in past work for the extraction of actinides from irradiated targets, using tri-butyl phosphate as an extraction medium. However, tri-butyl phosphate does not easily discriminate between uranium, neptunium and plutonium.

If other species are considered, hydrophobic alcohols, ethers and ketones are of particular interest. It is proposed that their extraction properties arise due to the linear structure of the uranyl cation with the overall positive charge residing conventionally on the central uranium atom - ie the uranium atom is $\delta^+$. As such, it is open to bonding with $\delta^-$ atoms in organic compounds. Most common among these are the amines, alcohols, ethers and ketones.

However most of these compounds are highly soluble in water and are thus not sufficient for solvent extraction of uranium from aqueous solution. This can be remedied by the use of compounds with long-chain alkyl groups, although they may suffer from poor extraction capabilities due to steric hindrance between the long alkyl chains and the large $\text{UO}_2^{2+}$ species. Possibilities here include 2,4-dimethyl-pentan-3-ol (sometimes called di-isopropyl carbinol in older literature), ethoxyethane (diethyl ether) and (1-methyl)ethoxy(1-methyl)ethane (or di-isopropyl ether, DIPE). All of these compounds have a limited solubility in water.
There is a need to extract $^{236}$Np with good recovery (>90%) from irradiated uranium targets with fission products being present in >100 MBq quantities (i.e. 100-1000 ng, or $10^{14}$-$10^{15}$ atoms) (Larijani, et al, 2015), whilst at the same time recovering as much uranium as possible and also recovering $^{236}$Pu where possible. Isotopically pure target uranium (unless it is natural uranium) is difficult and expensive to obtain, and in any case NPL must provide a complete mass balance for EURATOM reporting purposes. The amount of uranium in a target may vary between 0.5 and 1.5 grams (i.e. ~1.2 - 4.0 × $10^{21}$ atoms). It was also planned that the $^{236}$Pu would be recovered, in expected 100-1000 kBq quantities (i.e. ~5-50 ng, or $10^{13}$-$10^{14}$ atoms) as it has commercial value (if pure enough) as a chemical yield tracer. However, the main product of interest in the current work is $^{236}$Np.

3.2.4 Neptunium chemistry in aqueous solution

3.2.4.1 Oxidation states of neptunium ions

The chemical properties most important for the analytical chemistry of neptunium in aqueous solutions are the variable valences of neptunium (Katz, et al, 1986; Adloff and Guillaumont, 1989). The chemistry is complex in that Np in aqueous solution consists as ions of five easily changeable oxidation states (3$^+$ to 7$^+$) (Thakur and Mulholland, 2012). The complexity arises in the changing oxidation states, causing significant issues in the chemical separation techniques outlined later on in this chapter. The affinity and distribution coefficient of neptunium for resin or solvent extraction strongly depends on the oxidation state of neptunium (Thakur and Mulholland, 2012).

Factors such as the acidity of the solution, presence of complex forming ligands, oxidants or reductants and the concentration of neptunium itself in solution all play a significant role in determining the oxidation state of neptunium ions in solution. As per Kihara, et al, (1999) Np$^{3+}$
and Np\(^{4+}\) exist in acidic solutions without ligand, whereby Np\(^{3+}\) is quickly oxidized to the 4\(^{+}\) due to oxidation with atmospheric oxygen. Pentavalent neptunium ion Np (V) is the most stable oxidation state in solution (Yoshida, et al, 2006) as the pentavalent ion forms strong Lewis acids, which in turn form neptunyl, NpO\(_2\)\(^{+}\) species in acidic solution. However Np (V) undergoes disproportionation reaction forming Np (IV) and Np (VI) under acidic conditions (Adloff and Guillaumont, 1989):

\[
2\text{NpO}_2^{+} + 4\text{H}^{+} \leftrightarrow \text{Np}^{4+} + \text{NpO}_2^{2+} + 2\text{H}_2\text{O} \ (Equation \ 3.7)
\]

This makes Np (V) challenging to work with for this reason but also due to its low sorption on any resin (Yoshida, et al, 2006). Redox agents can be used to control the oxidation state of Np ions in aqueous media. In most of the EICHROM methods based on extraction chromatography, Np is eluted from the resin by moderate to strong acids in combination with a complexing agent such as ascorbic acid (C\(_6\)H\(_8\)O\(_6\)) or sodium nitrite (NaNO\(_2\)) in order to achieve redox control to perform the optimum chemical separation of Np, in order to ensure Np is eluted in the correct fraction (Table 3.3). Sodium nitrite adjusts the oxidation states of Pu to IV\(^{+}\) and V\(^{+}\) in the case of Np. Thus such an agent can oxidise tetravalent Np to the pentavalent state and at the same time reduce hexavalent Np. As both Pu and Np can exist in several oxidation states at the same time, sodium nitrite is significant for when only one oxidation state is needed. As the V\(^{+}\) state is a non-extractable species (Yoshida, et al, 2006), if Np is then oxidised into the hexavalent Np-species, NpO\(_2\)\(^{2+}\), behaves as the chemical analogue of UO\(_2\)\(^{2+}\), or if reduced to Np\(^{4+}\) behaves as a chemical analogue of Pu\(^{4+}\), and thus both Np and Pu can be separated from the initial aqueous phase.
Figure 3.7 - complexing agent ascorbic acid (C₆H₈O₆).

<table>
<thead>
<tr>
<th>Oxidation state of Np ion</th>
<th>Procedure</th>
<th>Agents</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before treatment</td>
<td>After treatment</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Oxidative treatment</strong></td>
<td>Np (VI)</td>
<td>Ce(IV)</td>
<td>HNO₃, H₂SO₄</td>
</tr>
<tr>
<td>Np (III), Np (IV), Np (V)</td>
<td></td>
<td>MnO₄⁻</td>
<td>HNO₃, H₂SO₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ag (II)</td>
<td>1M HClO₄</td>
</tr>
<tr>
<td>Np (III)</td>
<td>Np (IV)</td>
<td>O₂</td>
<td></td>
</tr>
<tr>
<td><strong>Reductive treatment</strong></td>
<td>Np (IV)</td>
<td>Fe²⁺</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Np (V), Np (VI)</td>
<td></td>
<td>I⁻</td>
<td>5M HCl</td>
</tr>
<tr>
<td>Np (VI)</td>
<td>Np (V)</td>
<td>NH₂NH₂</td>
<td>1M H⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NH₂OH</td>
<td>1M H⁺</td>
</tr>
<tr>
<td>Np (IV), Np (V), Np (VI)</td>
<td>Np (III)</td>
<td>Zn (Hg)</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.3 - Further examples of redox agents used to adjust oxidation states of Np ions in aqueous solutions (Thakur and Mulholland, 2012).

3.2.4.2 Literature review of the radiochemical separation methods for Np

Reprocessing of spent nuclear fuels to recover reusable uranium and plutonium and the partitioning of high-level radioactive liquid wastes (HLW) constitute the main processes of the nuclear fuel cycle (Thakur and Mulholland, 2012). The separation of $^{237}$Np is one of the major components of the PUREX process and high level waste. A literature study indicated that solvent extraction, ion-exchange chromatography and extraction chromatography have all been
used to separate Np ions (Yoshida, et al, 2006). Most separation methods control of neptunium ion oxidation states which varies between $3^+$ and $6^+$ and utilization of specific chemical behaviour of the ion in each oxidation state (Burney and Harbour, 1974; Choppin and Nash 1995). In the current work the key separations that are required, are to isolate Np from the natural uranium target, and the fission products produced as part of the target irradiation and to make sure that Np is converted to the $+IV$ oxidation state. Once the redox control is complete in most of the solvent extraction and chromatographic methods Np is eluted from the resin or solvent by moderately to strong acid or in combination with a complexing agent.

### 3.2.4.2.1 Solvent Extraction

Many extractants such as 2-thenoyltrifluoroacetone (HTTA) and tri-n-butyl phosphate (TBP) have been widely used for the extraction of neptunium (Laskorin, et al, 1985; Rozen and Nikolotova, 1998; Geary, 1955). The PUREX process for the reprocessing of spent fuel throughout the world, whereby U (VI) and Pu (IV) are extracted from an aqueous solution 2-3 M HNO$_3$ into an organic solution of 30% TBP in kerosene (Musikas and Schulz, 1992). However due to the difficulties in controlling the oxidation state of neptunium, different oxidation states of neptunium form in changing chemical environments, leading to the distribution of neptunium in different fractions of the PUREX process (Taylor, et al, 1997).

$\beta$-diketones, HTTA are widely used (Rozen and Nikolotova, 1998; Holm, 1981; Lindahl, et al, 2004). Moore (1957) developed a procedure to separate trace amounts of neptunium ions in the presence of fission products, plutonium and uranium isotopes. Separation of plutonium was carried out by reducing plutonium to Pu (III) by using a suitable reducing agent, since neptunium predominantly exists as Np (IV), the method showed chemical recoveries of 99%.
Zantuti, et al, (1990) developed a method for the separation of trace levels of neptunium ions from nitric acid, containing much larger quantities of uranium using the synergistic extraction with 1-Phenyl-3methyl-4-benzoyl-pyrazol-5-one (HPMBP) and di-2-ethylhexylphosphoric acid. Mohapatra and Manchanda, (1993) used 3-phenyl-4-bezoyl-5-isoxazolone to extract Np (IV) for the separation ²³⁷Np from ²³⁶Pu and uranium target material.

3.2.4.2.2 Ion-Exchange chromatography

Various methods based on ion-exchange chromatography methods have been used to separate Np ions (Burney and Harbour, 1974). As discussed above, the redox control of neptunium and plutonium is key for radiochemical analysis with an anion exchange column because the distribution coefficients of plutonium and neptunium are dependent on their oxidation states (Thakur and Mulholland, 2012; Katz, et al, 1986). Chemical separation of neptunium commonly occurs using HNO₃, however it can also be performed using HCl (Maiti, et al, 1992), as the distribution coefficient for neptunium is large in high concentrations of HCl (Katz, et al, 1986). According to Thakur and Mulholland, (2012) the common procedure in separating neptunium using anion exchange is to adjust neptunium to the IV and the consequent absorption of the Np (IV) nitrate complex, i.e. Np(NO₃)⁶⁻ on the resin from 8 M nitric acid in the presence of 0.1 M sodium nitrite and recovering neptunium in the ⁴⁺ oxidation state by elution with 0.3 M nitric acid.

Various authors (Henley, 1989; Holm and Fukai, 1977) have used anion exchange resin (Bio-Rad AG1-X8, 100-200 mesh) columns to adsorb uranium, neptunium and plutonium using HNO₃. Fission products tend not to adsorb on anion resin under these conditions, so the AG1 resin column was thoroughly washed with further 8 M nitric acid to remove fission products (Harvey and Thurston, 1988). Plutonium was removed from the column with 12 M
hydrochloric acid that was also 0.1 M with respect to ammonium iodide (Harvey and Thurston, 1988), and the column thoroughly washed with additional 12 M hydrochloric acid to remove residual iodide ion. Neptunium was removed with 4 M hydrobromic acid (Marsh, et al, 1978) and reserved for measurement.

3.2.4.2.3 Extraction chromatography

Due to the high selectivity for the actinides, extraction chromatography has been studied by many authors to separate neptunium (Horwitz, et al, 1995; Maillard, et al, 2012; Guérin, et al, 2011; Jerome, et al, 2014). A number of authors have used TEVA resin for the successful separation of $^{237}$Np for ICP-MS measurements (Rollins, et al, 2009; Kenna, 2002; Baglan, et al, 2002). These authors have used ascorbic acid and iron sulfamate to adjust the oxidation state for neptunium. Although neptunium displays a number of oxidation states, the Np$^{4+}$ ion is not stable in acid solution and may be oxidised to Np$^{5+}$ in the presence of nitric acid. However, the Np$^{4+}$ ion is retained by TEVA extraction chromatography resin (Horwitz, et al, 1995); in 2.5 M HNO$_3$, the Np$^{4+}$ ion has a distribution coefficient ($k_d$) of ~5 000 and may be stabilised by reduction with ascorbic acid in the presence of the ferric ion, Fe$^{3+}$ (Strišovská, et al, 2013). Under the same conditions, the $k_d$ for Pu$^{4+}$ is ~30 000. An additional advantage of using TEVA for the separation of neptunium from the target material is the fact that uranium shows less tailing on TEVA resin than conventional ion-exchange resin (Thakur and Mulholland, 2012).

3.2.4.2.4 Combined radiochemical procedures for determination of Np and other actinides

Radiochemical separation of neptunium can sometimes require a two-step process (Thakur and Mulholland, 2012). Solvent extraction is commonly combined with another separation procedure (Coleman, 1965). Ayranov, et al, (2005a) reported a method of separation uranium
and neptunium using a complication of cyclohexane extraction and TRU and TEVA column separation. Horwitz et al (1995) used different extraction chromatography columns such as TEVA and TRU, in order to separate actinides. Maxwell developed a rapid separation method of all actinides and Sr in soil (Maxwell, 2006) using UTEVA and TEVA columns in tandem.

### 3.2.5 Principle and uses of radioactive tracers

In 1913 De Hevesy and Paneth were the first to carry out experiments with radioactive tracers using one of the naturally occurring radioactive isotopes of Pb to analyse the behaviour of Pb salts. While it is not always necessary to use radioactive isotopes for tracer studies (such as measurement of stable elements in mass spectrometry), the current work was focussed on producing a radioactive tracer for Np analysis. The choices available for a suitable Np tracer are constrained (Jerome, et al, 2014), one can use a Pu yield tracer such as $^{236}$Pu (Maxwell, et al, 2011; Thakur and Mulholland, 2012). However, with the complex chemistry of the actinide series, there is always the risk of speciation of Pu and Np during the analysis.

In selecting an isotope dilution tracer, a number of requirements must be met (Harvey and Lovett, 1984):

- The tracer must exhibit the same chemical behaviour as the analyte, and thus the tracer should be same element as the analyte,
- The tracer should not interfere with the measurement of the analyte or that the tracer does not register in the analyte measurement (and vice versa), and
- That chemical equilibrium between the tracer and analyte should be established at the earliest possible point in the analysis. This requires that the tracer should be added as soon as possible in the analysis and (for solids) employ total dissolution.
Furthermore, one should also consider that:

- The tracer should not be initially present in the samples being analysed, since using nuclides present in the samples being analysed complicates analysis,

- The tracer should be pure and not introduce contamination into samples being measured, especially the analyte. This puts astringent purity requirement on the tracer that may differ for mass spectrometry and radiometric measurements, and

- The tracer activity should be traceable to national or international standards, although this may not be necessary where the yield can be determined by comparative measurements, such as $\gamma$ emitting tracers.
Chapter 4

4. Metrological Techniques in Radionuclide Analysis and Measurement

In order to determine the radionuclide content of a sample it is necessary to prepare sources in a suitable form for radiometric (α and γ) and mass measurements. The physical and chemical form of the source must be selected to be compatible with the chosen technique. The form of the source should be readily reproducible for consistency and calibration purposes.

The research carried out in this thesis uses the following metrological techniques:

- γ-ray spectrometry
- α-particle spectrometry
- Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
- Scanned Electron Microscopy

4.1 Radiation Detection

The basis of all radiation detectors is a material that impinging radiation is transferred and is deposited into the detector material (Knoll, 2010). This creates an electrical signal that can then be analysed and measured to determine the properties of the incoming radiation. The most significant types of detectors used in work were semiconductor materials; High-purity Ge (HpGe) detector in γ-ray spectrometry and a surface barrier silicon detector for α-particle spectrometry.

4.1.1 Semiconductor materials

Solid-state detectors operate by exploiting the presence of an electronic band gap in a semiconductor. These energy bands are divided into two groups, namely the conduction and valence
bands. Incident energy imparts energy to a solid-state detector to promote electrons into the conduction band of the material (Figure 4.1), which leads to a change in conductivity of the material; the size of the conductivity change is a function of the incoming energy.

\[ E_g \sim 1 \, \text{eV for semiconductors} \]

[Figure 4.1- Band structure in a semiconductor (Gilmore, 2011).]

For some semiconductors, such as silicon or germanium, thermal energy at 298 K (Gilmore, 2011) is sufficient to achieve a change in conductivity, necessitating cooling to a suitable (lower) temperature. The interaction cross section for γ rays increases with (i) atomic number, (ii) bulk density and (iii) volume, and so detector systems maximise detection efficiency by using (relatively) high atomic number materials with (relatively) high density and large volume. The use of semiconductor materials such as hyper-pure crystalline germanium which is widely used in γ ray measurements or silicon (for α-particle spectroscopy) is the only way to reduce the statistical limit on energy resolution by increasing the number of information carriers per pulse, thus resulting in a much larger number of carriers for a given incident radiation event than is possible with any other common detector type. In this case the
fundamental information carriers are electron-hole pairs created along the path taken by the charged particle (primary radiation or secondary particle) through the detector. Their motion in an applied electric field generates the basic electrical signal from the detector.

There are two types of semiconductor to be considered; p-type and n-type, based on having either a majority impurity concentration of electrons or holes respectively. It is referred to as a p-type when it has an excess of holes and n-type when in excess of valence electrons. The contact between the two regions creates a depletion layer where the excess charge carriers cancel each other. This layer is electrically neutral, sensitive to radiation and is the active medium for semiconductor detector. The depleted region is normally very thin and when the n-region is connected to a positive terminal while the p-region to the negative terminal, the size of the depletion layer increases with an applied voltage resulting in what is known as a reverse-biased junction (Gilmore, 2011). The junction effectively increases the electric field in the depleted zone and thus the rate and efficiency of collection by charge carriers at the electrode also increases (Knoll, 2010).

4.2 Gamma ray interactions with matter

A γ-ray spectrometer is a non-destructive instrument that provides information on both the energy and intensity of radiation that is emitted from γ ray (or energetic X-ray) sources. The perfect gamma-ray spectrometer array combines excellent spectral selectivity (i.e., good energy resolution), excellent timing characteristics and sufficient detection efficiency (Eberth & Simpson, 2008). However, no detector material encompasses all of these attributes. A major limitation of scintillation detectors is their relatively poor energy resolution; germanium detectors can offer resolutions down to a few tenths of a percent, in comparison NaI(Tl) scintillation detectors have $\Delta E / E$ or $FWHM / E$ values of ~5-10%. For this reason, the full-
energy peaks obtained from the sodium iodide detector may have an interference from other transitions, hence why germanium detectors have properties (Table 4.1) that have led them to becoming the prominent detector type used in radionuclide metrology.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Germanium Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Number (Z)</td>
<td>32</td>
</tr>
<tr>
<td>Atomic Weight (A)</td>
<td>72.60</td>
</tr>
<tr>
<td>Density (300K) g/cm³</td>
<td>5.32</td>
</tr>
<tr>
<td>Forbidden energy (band) gap in eV</td>
<td></td>
</tr>
<tr>
<td>300 K</td>
<td>0.665</td>
</tr>
<tr>
<td>0 K</td>
<td>0.746</td>
</tr>
<tr>
<td>Electron mobility cm²/V s</td>
<td></td>
</tr>
<tr>
<td>300 K</td>
<td>3900</td>
</tr>
<tr>
<td>77 K</td>
<td>36000</td>
</tr>
<tr>
<td>Hole mobility cm²/V s</td>
<td></td>
</tr>
<tr>
<td>300 K</td>
<td>1900</td>
</tr>
<tr>
<td>77 K</td>
<td>42000</td>
</tr>
<tr>
<td>Energy per electron hole pairs in eV</td>
<td></td>
</tr>
<tr>
<td>77 K</td>
<td>2.96</td>
</tr>
</tbody>
</table>

Table 4.1- Intrinsic properties of germanium crystals (Knoll, 2010).

Ideally, a γ-ray spectrometer would have a response function consisting of only the full-energy peak at energies $E_γ$, with no continuum or background. Typically, energies for γ ray photons are between ~10 keV to ~10 MeV. The interaction of photons ($\gamma$ and X-rays) with detection media proceeds via three main processes: photoelectric absorption, Compton scattering and pair-production (Figures 4.2 and 4.3). Each of these processes lead to the partial or complete transfer of the γ ray photon energy to electron energy (Vetter, 2007). They result in sudden and abrupt changes in the γ ray photon, in that the photon either disappears entirely or is scattered through a significant angle as in the case of Compton Scattering. In the low-energy region,
discontinuities in the curve or "absorption edges" appear at γ ray energies that correspond to the binding energies (11.1 keV for germanium (Gilmore, 2008)) of electrons in the various shells of the absorber atom.

Figure 4.2- Main interactions of photons with detection media as a function of energy (Krane, 1998).
Figure 4.3- Mass attenuation coefficient of germanium for photons with energies from 10 keV → 10 MeV (XCOM: Photons Cross Sections Database, NIST).
4.2.1 Photoelectric Absorption

The photoelectric effect is the predominant attenuation mechanism for photon energies in the range $\leq 150$ keV for germanium. In photoelectric absorption, the energy of the photon is wholly transmitted to a bound orbital electron of an atom of the absorbing medium (usually from an inner shell), resulting in the ejection of a photoelectron with a kinetic energy equal to that of the photon less the associated electron binding energy and the disappearance of the original photon. The resulting excited atom may be de-excited by the emission of Auger electrons or a characteristic X-ray photons which may in turn interact with the absorbing medium. Further re-absorption from photoelectric processes continues until, ideally, all of the energy of the gamma ray is absorbed within the detector, which contributes to the total energy peak. The energy level from which the atomic electron is ejected depends upon the energy of the incoming gamma ray. The ejection of electrons primarily take place in the K shell but if the energy is not sufficient enough to eject the K electron, then electrons in the L or M shell will be ejected instead.

4.2.2 Compton Scattering

Compton scattering occurs when the incident photon scatters from a free electron in the absorber medium with only a partial transfer of energy. The initial photon is scattered and re-emitted in a different direction with a reduced energy, together with a recoil electron. The energy transfer is dependent on the scattering angle and may be determined by the following equation (assuming the electron is free and at rest).

\[
E'_\gamma = E_\gamma \frac{E_\gamma}{m_0 c^2 (1 - \cos \theta)} \quad (Equation 4.1)
\]
\( E_\gamma \) is the energy of the incident particle, \( m_0c^2 \) is the rest mass energy of the electron and \( \theta \) is the angle which the photon is scattered. When \( \theta = 0^0 \), the photon is forward (i.e. not scattered at all) and Equation 4.1 reduces to \( E_\gamma = E'_\gamma \). When the \( \gamma \) ray is back-scattered such that \( \theta = 180^0 \) the terms in the bracket (Equation 4.2) would still be \(< 1\) and thus only a fraction of the \( \gamma \) ray energy will be transferred to the recoil electron.

The probability of a photon Compton Scattering at an angle \( \theta \) is given by the Klein-Nishina formula (Klein and Nishina, 1929):

\[
\frac{d\sigma_c}{d\Omega} = r_0^2 \left[ \frac{1}{1 + \alpha (1 - \cos \theta)} \right]^3 \left[ \frac{1 + \cos \theta}{2} \right] \left[ 1 + \frac{\alpha^2 (1 - \cos \theta)^2}{(1 + \cos^2 \theta)(1 + \alpha (1 - \cos \theta))} \right] \quad (Equation \ 4.2)
\]

where \( \alpha \) is the photon energy and \( r_0 \) is the electron radius.

### 4.2.3 Pair Production

This interaction process takes place when the incoming photon has an energy greater than twice the electron rest mass, i.e., \( 2m_0c^2 = 1.022 \) MeV, as given shown by:

\[
E_\gamma = 2m_0c^2 + E_{e^-}^{kin} + E_{e^+}^{kin} \quad (Equation \ 4.3)
\]

where \( E_\gamma, m_0, \) and \( E_{e^-} \) are the incoming \( \gamma \)-ray energy, rest-mass of an electron, speed of light, and the kinetic energy of the electron, respectively.
In the process of pair-production the original photon is destroyed and is replaced by an electron-positron pair. The process is predominantly confined to very high energy photons and is energetically impossible below incident photon energies of 1.022 MeV (Vetter, 2007). The interaction must take place within the Coulomb field of an atom in order to preserve both energy and linear and angular momentum and the positron and electron share any excess energy as kinetic energy. Once the positron has slowed sufficiently in the local medium, it eventually annihilates with an atomic electron from the medium producing two 511 keV photons in opposing directions. The original pair production interaction and the annihilation radiations are in virtual coincidence because the time required for the positron to slow down prior to annihilation is only of the order of 1 ns (Vetter, 2007). For a standard size of detector, the electron and positron kinetic energies are typically fully deposited whereas the annihilation photons may either escape the detector volume, or undergo further interactions within the detector. These additional interactions may lead to either partial or complete energy absorption of the residual γ ray energy. When one of the two annihilation γ rays escapes from the detector volume without further interaction, 0.511 MeV will be lost from the detector. Therefore, a separate peak will present in the spectrum with an energy level of $E_γ - 0.511$ MeV, called the single-escape peak, where $E_γ$ is the γ ray energy characterised by the full-energy peak. If both of annihilation γ rays escape from the detector without interaction this contributes to the double escape peak at the energy level of $E_γ - 1.022$ MeV.

4.2.4 High purity Ge operational characteristics

4.2.4.1 Background radiation in γ ray detection

Gamma-ray spectroscopy of all environmental NORM samples and weak (<1 kBq) radioactive sources (Knoll, 2010) can require long counting times to achieve the required counting
statistics and sensitivity. Thus, it is of significance to understand the background present in a laboratory before measurement of samples.

**Cosmic radiation**- secondary radiation from cosmic ray interactions including both fast neutrons and high-energy muons are of significance to the background of most measurement laboratories (with the exception of underground laboratories) (Brodziniski, *et al*, 1988). The interaction of muons with high-\(Z\) materials such as lead (which is often used as shielding) can also produce secondary neutrons, which affect the background of the detector. Some of the radionuclides that are produced by interactions with cosmic radiation and atmosphere, detector and shielding materials are listed in Table 4.2.

**Terrestrial radiation**- Terrestrial or primordial radioisotopes can be found in the building material that form the laboratory, cryostat, detector build and shielding. Lead shielding which is used in the coffins that house the detectors, which may also contain the radioactive isotope lead, \(^{210}\)Pb; the activity levels of this are typically up to 500 Bq/kg (Landsberger and Millsap, 2014). NPL has a detector set up which will be explained in chapter 5 of this thesis that has a significant lower background, which is of importance for the measurement of the NORM reference materials in this work.

**Compton and Fluorescence scattering**- The shielding used in an experimental set up, which is mostly made up of lead can become ionised or excited by impinging radiations, and then deexcite emitting a characteristic X-ray. Lead has a characteristic \(K_x\) and \(K_\beta\) rays between 74-85 keV. In addition, the lead is also typically shielded with a liner of low \(Z\) material such as cadmium \((Z = 48)\) or tin \((Z = 50)\), which emit \(K_x\) and \(K_\beta\) rays between 23-29 keV.
<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>Isotope &amp; Reaction</th>
<th>Source of interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>53.5</td>
<td>$^{73m}$Ge</td>
<td>$^{72}$Ge (n,$\gamma$) in detector crystal</td>
</tr>
<tr>
<td>66.6</td>
<td>$^{73m}$Ge</td>
<td>$^{72}$Ge (n,$\gamma$) sum 13.1 + 53.5 keV, in crystal</td>
</tr>
<tr>
<td>139.7</td>
<td>$^{75}$Ge</td>
<td>$^{74}$Ge (n,$\gamma$) in detector crystal</td>
</tr>
<tr>
<td>198.4</td>
<td>$^{71m}$Ge</td>
<td>$^{70}$Ge (n,$\gamma$) sum 175.0 + 23.4 keV, in crystal</td>
</tr>
<tr>
<td>477.6</td>
<td>$^{10}$B (n,$\alpha$)</td>
<td>Reactions with trace amounts of boron, $^7$Li and $^7$Be produced via decay of cosmogenic radiation in the atmosphere</td>
</tr>
<tr>
<td>511.0</td>
<td>Annihilation</td>
<td>$\beta^+$ emitters, $&gt;$ 1.022 MeV $\gamma$ rays, $^{232}$Th NORM decay chain + pair production following 2.614 MeV $\gamma$ in $^{208}$Tl decay.</td>
</tr>
<tr>
<td>537.4</td>
<td>$^{206}$Pb (n,n')</td>
<td>Reactions in lead</td>
</tr>
<tr>
<td>558.4</td>
<td>$^{114}$Cd (n,n')</td>
<td>Reactions in cadmium</td>
</tr>
<tr>
<td>569.7</td>
<td>$^{207}$Pb (n,n')</td>
<td>Reactions in lead</td>
</tr>
<tr>
<td>595.9</td>
<td>$^{74}$Ge (n,n')</td>
<td>Reactions in Ge crystal, $^{74}$Ge ($^2$+)</td>
</tr>
<tr>
<td>669.6</td>
<td>$^{63}$Cu (n,n')</td>
<td>Reactions in copper</td>
</tr>
<tr>
<td>691.5</td>
<td>$^{72}$Ge (n,n')</td>
<td>Due to recoil summation $^0$$\rightarrow$$^0$</td>
</tr>
<tr>
<td>718.3</td>
<td>$^{10}$B (n,n')</td>
<td>Reactions with trace amounts of boron.</td>
</tr>
<tr>
<td>803.1</td>
<td>$^{206}$Pb (n,n')</td>
<td>Reactions in lead, inelastic neutron scatter</td>
</tr>
<tr>
<td>834.0</td>
<td>$^{72}$Ge (n,n')</td>
<td>Due to recoil summation</td>
</tr>
<tr>
<td>843.8</td>
<td>$^{27}$Al (n,n')</td>
<td>Reactions in aluminium</td>
</tr>
<tr>
<td>846.8</td>
<td>$^{59}$Fe (n,n')</td>
<td>Reactions in iron</td>
</tr>
<tr>
<td>962.1</td>
<td>$^{63}$Cu (n,n')</td>
<td>Reactions in copper</td>
</tr>
<tr>
<td>1014</td>
<td>$^{27}$Al (n,n')</td>
<td>Reactions in aluminium</td>
</tr>
<tr>
<td>1039</td>
<td>$^{70}$Ge (n,n')</td>
<td>Due to recoil summation</td>
</tr>
<tr>
<td>1369</td>
<td>$^{27}$Al (n,$\alpha$')</td>
<td>Reactions in aluminium</td>
</tr>
<tr>
<td>1779</td>
<td>$^{27}$Al (n,$\gamma$')</td>
<td>Reactions in aluminium</td>
</tr>
<tr>
<td>2223</td>
<td>$^1$H (n,$\gamma$) $^2$H</td>
<td>Reactions in hydrogenous material, Q-value for deuterium from p + n → $^2$H</td>
</tr>
<tr>
<td>2312</td>
<td>$^{14}$N (n,n')</td>
<td>Reactions in nitrogen gas near detector i.e. air</td>
</tr>
<tr>
<td>4439</td>
<td>$^{12}$C (n,n')</td>
<td>Reactions in carbon near the detector i.e. air</td>
</tr>
<tr>
<td>5106</td>
<td>$^{14}$N (n,n')</td>
<td>Reactions in nitrogen gas near detector i.e. air</td>
</tr>
<tr>
<td>6129</td>
<td>$^{16}$O (n,n')</td>
<td>Reactions in oxygen gas near the detector i.e. air</td>
</tr>
<tr>
<td>7115</td>
<td>$^{16}$O (n,p)</td>
<td>Reactions in oxygen gas near the detector</td>
</tr>
<tr>
<td>7416</td>
<td>$^{70}$Ge (n,n')</td>
<td>Reactions in oxygen gas near the detector</td>
</tr>
<tr>
<td>10199</td>
<td>$^{73}$Ge (n,n')</td>
<td>Reactions in oxygen gas near the detector</td>
</tr>
</tbody>
</table>

Table 4.2- Common $\gamma$ rays observed in background spectra as a result of cosmic radiation, compiled from, Brodzinski, et al, 1988.

### 4.2.4.2 Gamma-ray attenuation and shielding

Gamma-ray attenuation describes the process by which photons are removed from a “pencil photon beam” (Krane, 1998) through a defined thickness of material. For $\gamma$ radiation, due to its...
zero mass and charge has a high penetration power in matter in comparison with $\alpha$ and $\beta$ particles. Increasing the thickness of the absorber only gives a higher probability of the loss of $\gamma$ radiation through the interaction processes (i.e. by either absorption or scattering).

The basic attenuation of photons is given by Beer-Lambert Law (Beer, 1852), which is:

$$I(t) = I_0 e^{-\mu t} \quad (Equation \ 4.4)$$

where $I$ = transmitted photon intensity, $I_0$ = incident photon intensity, $e$ = base of the natural logarithm system, $\mu$ = the linear attenuation coefficient and $t$ = thickness of the absorber material.

The mass attenuation coefficient of this interaction, denoted by $\mu_m$, depends on the energy of the incoming $\gamma$ ray photons and not on the physical state of a given absorber and can be expressed as:

$$I = I_0 e^{-\mu_m \rho t} \quad (Equation \ 4.5)$$

where $\rho t$ is the density of the mass thickness of the absorber in g/cm$^3$.

For the low-level radioactivity measurements such as the NORM measurements carried out in this thesis (Chapter 5), an environmental sample was usually prepared in a finite volume which may give rise to significant $\gamma$-ray attenuation within the sample volume itself (i.e. “self-attenuation”). Thus the determination of $\gamma$-ray attenuation with matter is important in assessing the effectiveness of $\gamma$-ray shielding and to correct for self-absorption within the sources,
provided the mass attenuation of the matrix material is known (Gilmore, 2011). This depends on several factors such as the $\gamma$-ray energy, the geometry and the type and/or density of the sample itself, and correction has to be made in the course of the analysis (especially for the NORM measurements, Chapter 5) (Brodziniski, et al, 1988).

4.2.4.3 Peak summation

Coincidence or cascade summing (hereafter referred to as summing) occurs when two or more $\gamma$ rays originating from decay cascade following a single disintegration results in a single ‘summed’ pulse. Summing can be distinguished as either being ‘true’ or random. True sum peaks occur for all coincident gamma rays that are detected including events which do not result in full-energy deposition such as scattered or Compton radiation. When two $\gamma$ rays sum, the apparent efficiency for each $\gamma$ ray is less than a $\gamma$ ray of the same energy with no coincidence summing. In addition to ‘true’ sum peaks, random sum peaks can occur due to the finite time resolution of the detection system. However, due to pulse pile up rejection in modern processing electronics this is of less importance (Evans, 1955).

In the case of true coincidence summing, where two $\gamma$ rays in a cascade are emitted since the excited nuclear states to which the $\alpha$ or $\beta$ particles decay have life times of the order of pico-seconds, it is probable that both $\gamma$ rays emitted in a single cascade can be detected within the resolving time of a $\gamma$-ray spectrometer. As a result of true coincidence summing, the detector accumulates the sum total of energy deposited by the cascading gamma rays from a given nuclear decay. Thus events are lost via summing-out or gained by summing-in from the Full Energy Peak of the $\gamma$ ray of interest, and any activity determination based on the Full Energy Peak will be in error. Therefore, it is important to correct for true coincidence effects when determining absolute detection efficiency and/or related totally activity measurements.
4.2.4.4 Characterisation

Full-peak detection efficiency and energy resolution are significant characteristics in the operation of a γ-ray spectrometer. Before any of the samples in the work are measured it is key that the detector used is accurately calibrated for efficiency and energy detection response. This is to avoid potential sources of calibration error, which include: energy shift, peak width, effect of source/detector distance, effects of sample density, inaccurate decay corrections, live-time corrections, (Gilmore, 2008).

4.2.4.5 Energy resolution

Observed peaks from a γ-ray spectrum have a finite width. The energy resolution of a detector depends on the electronic noise of the different elements of the amplification chain, but also on the statistical fluctuations in the number of electron-hole pairs created in the active detector volume. The energy resolution of the detector is expressed as the full width half maximum (FWHM) under the assumption at a near Gaussian response function for the lineshape, and can be obtained from a given spectrum. The total FWHM is defined as:

\[
FWHM = \sqrt{(FWHM)_{det}^2 + (FWHM)_{elec}^2} \quad (Equation \ 4.6)
\]

\( (FWHM)_{det} \) and \( (FWHM)_{elec} \) represent the detector and electronic contributions to the total FWHM. The resolution is generally expressed in keV for a germanium detector. Depending on the detector type, the resolution (FWHM) can get down to 1.9 keV at 1332 keV, 0.50 keV at 122 keV, and 0.15 keV at 5.9 keV implying an electronic noise contribution of <0.8, 0.22, and 0.10 keV respectively (Gilmore, 1998).
4.2.4.6 Efficiency calibration

The absolute full-energy peak efficiency of a detector \( \varepsilon_y \), is the measure of the probability (expressed in absolute values or as a per cent) (Gilmore, 1998) that a \( \gamma \) ray of energy \( E_\gamma \) is absorbed within the active volume of the detector. It depends on the solid angle \( \Omega \) of the detector viewed from the source and also the intrinsic factors that characterise the detector (such as the volume, mass and interaction cross section).

The two main efficiency parameters for a detector are the intrinsic and absolute efficiencies (Knoll, 2010). The intrinsic factors include energy-dependent fundamental effects, such as multiple Compton scattering/photoelectric effects, physical thickness and detector material. \( \varepsilon_{\text{intrinsic}} \) is the probability that a given photon of energy incident on the detector will be completely absorbed.

\[
\varepsilon_{\text{intrinsic}} = \frac{\text{number of pulses recorded at full energy peak}}{\text{number of } \gamma\text{-ray incident on the detector}} \quad (\text{Equation 4.7})
\]

The full-energy peak absolute efficiency \( \varepsilon_{\text{absolute}} \) is defined as the number of pulses recorded at a given interval in the full-energy peak (FEP), divided by the number of radiation quanta of that energy (particles or photons) emitted by a radiation source (in all directions) within the same interval (Ranger, 1999). This depends on the geometrical arrangements, primarily the distance from the source to the detector (Knoll, 2000; Gilmore, 2008). It is expressed as:

\[
\varepsilon_{\text{absolute}} = \frac{\text{number of pulses recorded at full energy peak}}{\text{number of radiation quanta emitted by a source}} \quad (\text{Equation 4.8})
\]
4.2.4.7 Experimental efficiency curve

In order to determine the source activity or $\gamma$-emission probability in a particular measurement, it is necessary to understand the detection efficiency for each peak observed in the spectrum. This can be carried out by mapping the detection efficiency curve versus $\gamma$-ray energy over a range of energies. Some National Metrology Institutes such as NPL, PTB (Germany) and NIST (USA) provide isotopes whose $\gamma$-ray emission rates have been calibrated to a precision ranging from 0.5 to 2.0% (Collins, et al, 2014). Single isotope sources provide a few well-separated $\gamma$ ray peaks whose peak area can be used to calibrate the detector efficiency at particular energies. If the energy scale must extend over a relatively wide range, a mixed-isotope source can be used, either sequentially or in combination. It is also important for the calibration measurements to have the same geometry as the actual samples. Thus the source-to-detector positioning ideally should be the same for the calibrations standards as for. In many cases it is not possible to produce samples that exactly match calibration standards in terms of geometry or matrix density and in this case mathematical methods through Monte Carlo computer modelling techniques are used (Wright and Kelsey, 2015). Packages that can be used include:

- MCNP (Monte Carlo N-Particle) (Briesmeister, 1997)
- GEANT (CERN Applications Software Group, 1994)
- SWORD (Software for Optimisation of Radiation Detectors, (Novikova, 2006))

These packages are extremely versatile (Gallardo, et al, 2013), however, it is important to provide detailed information about the structure of the detector. The models work most efficiently when the results are obtained by benchmarking the calibrations from the detector model against measurements with the calibration standards.
4.2.4.8 Energy calibration

When measuring γ rays the pulse height scale must be calibrated in terms of absolute gamma-ray energy if various peaks in the spectrum are to be properly identified. Accurate calibration should involve a standard source with γ-ray energies that are not widely different from those to be measured in the unknown spectrum. Once energy calibration points have been established over the entire energy range of interest, a calibration curve relating energy to channel number is normally derived. Common techniques involve the least-square of a polynomial of the form (Briesmeister, 1997), where:

\[ E_i = \sum_{n=0}^{N} a_n C_i^n \]  (Equation 4.9)

\( E_i \) is the energy corresponding to the channel number \( C_i \). A polynomial of order \( N = 2 \) is adequate for typical germanium spectrometers between 50 keV → 2.6 MeV, depending on the severity of nonlinearity that is present, which is often negligible.

4.3 Alpha-particle detection

Most modern alpha-spectrometers use Passivated Implanted Planar Silicon (PIPS) detectors which are formed via a combination of ion implantation and photolithography techniques (Crespo, 2012; Garcia-Torano, 2006). PIPS detectors introduce doped impurities at the surface of the silicon material by exposing \( n^+ \) or \( p^+ \) layers to a beam of ions produced by an accelerator. The steps begin with high-quality silicon that is mildly \( n \) type due to residual donor impurities. The front is \( p^+ \) type and is the rectifying contact, while the back part of the detector is \( n^+ \) type and is the non-injecting contact. The surface is then "passified" through the creation of an oxide layer at elevated temperature which leads to insulating regions on the surface which reduce leakage. Lithographic techniques are then used to produce multielectrode structures on single
wafers and remove selectively areas of the oxide where the entrance windows of the finished detectors are to be located. The junction is then formed by converting a very thin layer of silicon within the windows into $p$-type material through the implanting of acceptor ions ($B$) using an accelerator at 15 keV. To serve as a blocking electrical contact, the rear surface of the wafer is converted into $n+$ material through implantation of donor (As) ions at 30 keV. Annealing is then carried out at elevated temperatures to remove radiation damage with the process completed with aluminium being evaporated and patterned by photolithography to provide thin ohmic electrical contacts at the front and rear surfaces (Canberra.com).

PIPS detectors have several advantages over the formerly widely used surface barrier detectors (Garcia-Torano, 2006):

- Leakage current is one or two orders of magnitude lower than in surface barrier detectors, thus ensuring low noise operation and prevents microplasma breakdown, this is due to all junction edges being buried within the silicon wafer.
- Entrance windows (dead layer) are both rugged and stable and thus can be cleaned. The aluminized front surface is more rugged and less subject to damage compared with the gold front surface used in surface barrier fabrication.
- Contacts are ion-implanted to form thin, abrupt junctions for improved alpha resolutions in general but in particular at close detector-source spacing, which is of significance for counting statistics in environmental samples.
Alpha spectrometry is a radiometric technique that has found many applications in diverse fields such as characterization of nuclear wastes; (Arimoto, et al, 2005), environmental and geological studies (Crespo, 2012; Renteria Villalobos, et al, 2007), nuclear decay data measurements (Garcia-Torano, 2006) and those related to health and security (Yamamoto, et al, 2002; Minteer, et al, 2007). It utilises the PIPS detector, which is used for the quantitative determination of individual α emitting radionuclides, where typical energy resolution of 17 keV are achieved with a 450 mm² active area (Minteer, et al, 2007). Alpha-particles are rapidly attenuated by solids and thus sources need to be prepared to be thin and as uniform as possible to avoid attenuation and degradation (peak tailing and poor resolution) of the α spectrum (Crespo, 2012). As even air molecules attenuate α-particle energy, the measurements need to be performed under vacuum typically, <100 mTorr, where a bias voltage of up to -12V is applied across the PIPS detector. Alpha particles have characteristic energies typically between 4 and 8 MeV (Crespo, 2012), they are discrete, leading to distinguishable peaks in the α-emission spectrum, the energies of which can be used to identify specific nuclide decays. To quantify their activities, the count rates due to the constituent radionuclides present under each peak, corrected for background detection efficiency and low energy tailing (Crespo, 2012) can be used.
Figure 4.4- Alpha-Spectrometry chamber as used in this thesis, with the active surface facing downwards, possessed an active diameter of 23.9 mm, a total diameter of 32.0 mm, and a height of 12.3 mm.

4.4 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Although generally less frequently used than radiometric methods, measurement of anthropogenic and naturally occurring radionuclides by ICP-MS has increased significantly since Blair, et al, 1986 applied ICP-MS to the determination of naturally occurring uranium and thorium. Due to improvements in sample preparation methods and instrumental performance, ICP-MS displays low instrumental background found at m/z = 232 and 238 and offers a sensitive method (parts per trillion or parts per quadrillion levels) depending on the instrument model used for stable element and long-lived radionuclide measurements in aqueous and solid samples (Lariviere, et al, 2006). Although traditionally applied to long-lived radionuclides, particularly in the actinide series as the technique has advanced, the number of radionuclides measurable and the detection limits achievable have improved. Brown, et al, 1988 being the first reported attempt to measure $^{99}$Tc and $^{129}$I, and Kim, et al, 1989 measuring $^{239/240}$Pu and $^{237}$Np in soils, shortly after, where the long half-life and low specific activity means there is a high number of atoms to count relative to the rate of radioactive decay.
The following section outlines the differences between ion-counting and decay counting techniques as described earlier in the chapter, including the principles of the technique, the limitations of ICP-MS, and a description of the ICP-MS used in this work.

### 4.4.1 Ion-counting versus decay counting

Activity decreases at an exponential rate can be written in terms of the decay constant ($\lambda$). Radioactivity refers to the number of nuclear disintegrations per unit time, expressed as becquerels (Bq), where the decay counting instruments measure the product of the nuclear decay (Lariviere, et al, 2006). In contrast mass spectrometry measures the number of atoms of the radioanalytes.

As described earlier in Chapter 2, radioactive decay can be described as:

$$A(t) = \lambda N(t) \quad (Equation \ 4.10)$$

Therefore, knowing the value of $\lambda$, for the specific radionuclide studied, a correlation can be made in order to derive the number of atoms. $N$ is proportional to $m$ which is the mass of the analyte, in respect to Avogadro’s number ($N_A$) and molar mass (MM), which can be expressed as:

$$N = \frac{N_A \times m}{MM} \quad (Equation \ 4.11)$$

where $N_A = 6.022 \times 10^{23} \text{ atoms/mol}$
Thus by rearranging equations 4.11 and 4.12, the mass of the sample (grams) can be expressed in terms of the activity (Bq), molar mass (g mol\(^{-1}\)) and decay probability by using its half-life \(T_{\frac{1}{2}}\) (seconds) for that particular radionuclide by:

\[
m = \frac{A \times MM \times T_{\frac{1}{2}}}{ln2 \times N_A} \quad (Equation \ 4.12)
\]

The proportional relationship between the various parameters in Equation 4.12 demonstrates that ICP-MS is favourable for long-lived radionuclides such as \(^{238}\)U and \(^{232}\)Th, which have a very low specific activity (Kim, et al, 1989).

### 4.4.2 Principles of ICP-MS

ICP-MS uses a high temperature inductively coupled plasma (ICP) source to ionise atoms of elements in a given sample to charged positive ions. The ions are then separated by their mass-to-charge ratio using a quadrupole mass analyser, with the selected ions passing to the detector (Montaser, 1998). If similar analytical performance can be achieved in regards to accuracy and limit of detection, then ICP-MS has the advantage of short measurement times (~5 minutes per sample) and low sample volumes (<1 mL depending on the sample introduction system). As shown by García-Alonso, et al, 1995, Kim, 2005 and Lariviere, et al, 2006 ICP-MS has shown to compare favourably to radiometric measurements for a wide range of radioanalytes at various concentrations.

The most common type of ICP-MS is a quadrupole instrument (ICP-QMS), and the process can be split into the following parts:
- Sample introduction system
- Ionisation source (ICP)
- Interface
- Mass Analyser
- Detector

The instrument used in this project (Agilent 8800 triple quadrupole ICP-QQQ-MS) is also equipped with a collision-reaction cell, and an additional mass analyser positioned before the entrance to the collision-reaction cell; further details of the instrument will be described in section 4.4.9.

4.4.3 Sample introduction

The sample is introduced as an aqueous sample via an autosampler and peristaltic pump into the nebulizer, which generates an aerosol of fine droplets that passes onto the spray chamber (Figure 4.5). The spray chamber separates droplets by size, where only the smaller droplets driven by the argon gas pass into the plasma, and larger droplets are removed into a waste vessel, via a peristaltic pump. The spray chamber is kept at a constant low temperature (approximately 2 °C) to keep the droplet size and therefore ionisation efficiency uniform.
Figure 4.5- Diagram of a MicroMist nebuliser and Scott double pass spray chamber, as used in the Agilent 8800 (figure taken from Peter Keen MPhys dissertation, 2016).

4.4.4 Ionisation source (ICP)

ICP-MS generally uses argon as the plasma gas because of its high first ionisation energy, as well as its relatively low cost and high abundance compared with other noble gases. The ionisation source (Figure 4.6) is made up of a torch (consisting of three concentric quartz tubes), an induction coil and a RF generator. A spark from the coil introduces free electrons, which are accelerated by an oscillating magnetic field. A stream of argon gas is introduced, and collision with high energy electrons ionises Ar to Ar$^+$. There is also recombination of Ar$^+$ with free electrons, leading to an equilibrium of: Ar $\rightleftharpoons$ Ar$^+$ + e$^-$. This sustains the high temperature in the plasma (~6000 K) with sufficient energy to ionise argon (15.8 eV), and therefore the majority of elements in the periodic table. The sample from the spray chamber passes into the centre of the torch, where the sample is evaporated, atomised and ionised to form a beam of singly charged cations.
4.4.5 Interface region

As the ion beam passes from the atmospheric conditions of sample introduction to vacuum conditions of the mass spectrometer, the ion beam expands as a result of the reduction in pressure. The interface region acts to focus the ion beam onto the mass analyser through the use of a sample and skimmer cone, and a series of electrostatically controlled ion lenses held at a negative potential, which pull the ion beam through to the quadrupole and also prevent photons and neutrally charged particles from entering the mass analyser.

The interface region experiences a pressure reduction from atmospheric pressure (1-2 torr) to $10^{-3}$ torr via an intermediate vacuum between the sample cone and the skimmer cone. There is also further pressure reduction to $10^{-5}$ from the cones to the quadrupole (Thomas, 2001). The cones are typically made of nickel with small diameter (<1 mm) orifices, with the sample cone orifice being slightly larger than the skimmer orifice.
The cones can become blocked with solid deposits over time in high matrix samples, such as the matrices used in the NORM reference materials in this work. This will reduce instrument sensitivity over the course of a run, thus making the sample digest and chemical separation aspects of the process significant. It is recommended that samples have no more than 0.2% total dissolved solid (TDS) content (the Agilent 8800 has high matrix introduction (HMI) that allows up to 2.5% TDS to be handled).

4.4.6 Mass analyser

A quadrupole mass spectrometer consists of four parallel conductive rods under applied radiofrequency (RF) and DC potentials applied to the opposite pairs of the rods, thereby producing an electrostatic field between the spaces of the rods, which in turn acts as a sequential filter where ions of a single mass to charge ratio ($m/z$) pass through to the detector at any given time. The voltages in the rods can be changed for a specific mass-to-charge ratio ($m/z$), enabling multi-element measurement within a single run, with a scanning speed of up to 2400 atomic mass units (amu) per second.

4.4.7 Ion detector

A secondary electron multiplier (SEM) is a common detector type for ICP-MS. Ions that pass through the quadrupole are converted to negative ions via a conversion dynode, and then amplified through the SEM an ion strikes the first dynode, which then amplifies the signal, producing secondary electrons that pass on to the second dynode etc. The output is a measurable electronic signal in counts per second. By running standards of a known concentration, the counts per second and therefore concentration of radionuclide(s) in a sample can be calculated. Secondary electron multipliers can be dual mode, with pulse and analogue modes for low and high signals, respectively.
4.4.8 Collision and reaction cells

ICP-MS measurements can be affected isobaric, polyatomic and tailing interferences. A summary of these is found in Table 4.3. To overcome these interferences some ICP-MS instruments are equipped with a collision or reaction cell, commonly positioned between the ion optics and the mass analyser (Epov, et al., 2003). By using an inert gas such as helium or hydrogen, polyatomic interferences such as argide interferences can be removed. In comparison, a reaction cell introduces reactive gases such as O₂, N₂O and CH₄ to selectively remove isobaric and/or polyatomic interferences by forming reaction products (Tanner, et al., 2002).

<table>
<thead>
<tr>
<th>Interference</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobaric</td>
<td>Isotope with a similar mass to the radionuclide of interest</td>
</tr>
<tr>
<td>Polyatomic</td>
<td>Interferences formed by reactions of elements with gases in the plasma such as argides, oxides and hydrides</td>
</tr>
<tr>
<td>Tailing</td>
<td>Overlapping peak from an abundant isotope at a neighbouring mass to the radionuclide of interest such as ⁸⁸Sr on ⁹⁰Sr or ¹³³Cs on ¹³⁵Cs.</td>
</tr>
</tbody>
</table>

Table 4.3- Interferences impacting radionuclide measurement by ICP-MS.

The aim is to use a gas that only reacts with the analyte or the interference (Isnard, et al., 2006). When using a reaction gas, polyatomic interferences can potentially form e.g. oxides when using oxygen as a reactive gas (Zoriy, et al., 2005). Thus, the tailing signal cannot be separated between the analyte and a tailing signal from an abundant isotope of the same element.
4.4.9 Triple quadrupole ICP-MS

The ICP-MS used in the current work is an Agilent 8800 triple quadrupole ICP-QQQ-MS (Figure 4.7), which has been applied to measurements of multiple radionuclides including $^{135}\text{Cs}/^{137}\text{Cs}$, $^{236}\text{U}/^{238}\text{U}$, $^{127}\text{I}/^{129}\text{I}$ and $^{90}\text{Sr}$ (Ohno, et al, 2013, Tanimizu, 2013, Zheng, et al, 2014, Russell, et al, 2016). The Agilent 8800 is equipped with a collision/reaction cell positioned in front of a quadrupole mass filter. However, unlike other collision/reaction cell setups, there is an additional quadrupole positioned before the entrance to the cell termed the Octopole Reaction System (Figure 4.8).

Figure 4.7- Agilent 8800 ICP-QQQ-MS and ASX-500 autosampler.
The first quadrupole (Q1) provides a mass filter to the ion beam before entering the cell, which gives a greater control over the cell chemistry and products formed. For example, in the case of $^{90}\text{Sr}$, $\text{O}_2$ is used as a reactive gas to remove isobaric $^{90}\text{Zr}$. If Q1 is set to $m/z=90$, then $^{74}\text{Ge}^{16}\text{O}$ and $^{58}\text{Ni}^{16}\text{O}$ will not form because $^{74}\text{Ge}$ and $^{58}\text{Ni}$ will be removed by Q1 before entering the cell (Russell, 2016). The additional mass filter also offers greater abundance sensitivity compared to instrumentations with a single mass filter, with a theoretical value of $10^{-14}$ ($10^{-7}$ from each quadrupole) (Agilent, 2015), which provides improvements in the measurement of radionuclides that have significant tailing such as $^{236/238}\text{U}$ interferences (Tanimizu, 2013) and $^{127/129}\text{I}$ (Shikamori, et al, 2012) (Table 4.4).
<table>
<thead>
<tr>
<th>Instrument Mode</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Quad</td>
<td>Q1 acts as an ions guide, Q2 operating</td>
</tr>
<tr>
<td>MS/MS</td>
<td>Both Q1 and Q2 are operational</td>
</tr>
<tr>
<td>He</td>
<td>Helium is used as a collision gas</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen is used as a collision gas</td>
</tr>
<tr>
<td>Gas line 3</td>
<td>Corrosive gas (e.g. ammonia) used as a reaction gas</td>
</tr>
<tr>
<td>Gas line 4</td>
<td>Non-corrosive gas (e.g. oxygen) used as a reaction gas</td>
</tr>
</tbody>
</table>

Table 4.5- Possible ways the ICP-QQQ-MS can be setup to manipulate the signal of the ion beam.
The Octopole Reaction System can run both with or without gas and in single quad mode or MS/MS mode. In the two-varying gas modes the detector can be used to observe the effect that gases have on the abundance of the analyte but also any interferences. In single quadrupole mode, Q1 does not act as a quadrupole but as an ion lens to guide the ion beam towards Q2 through an inactive ORS. MS/MS mode on the other hand uses both Q1 and Q2 as quadrupoles. However, when in MS/MS mode the ion transmission is also reduced as the quadrupoles discriminate against both the ion’s m/z and kinetic energy. Thus, which mode is used is dependent on the aims of the measurement. Amr (2016) recently measured $^{90}$Sr, $^{137}$Cs, $^{238}$Pu, $^{239}$Pu and $^{240}$Pu using an Agilent 8800 to establish a baseline for global fallout in Qatar soil and sediments (Amr, et al, 2016). As referenced in that particular study in order to determine the low activity concentrations of the analytes of interest the instrument was operated in single quad mode (i.e. with only Q2 and no collision/reaction gas), it was determined that chemical separation was required prior to measurement. The critical tuning parameters were determined to be the ion optics voltages, nebuliser gas flow rate and RF power.

4.5 Scanning Electron Microscopy

In a scanning electron microscope, a high energy electron beam is restored across a small rectangular area on the surface of the sample. During this process atoms of the sample are ionized. The electrons ejected from the outer shells of the atoms (inelastic scattering) are collected by a secondary electron detector of the scanning electron microscope to form images which give topographic detail about the surface being scanned. Some high energy electrons are deflected through an angle very close to 180° (elastic scattering) and these are detected by a 4-quadrant back-scattered electron detector. These images show variation in the chemical composition of the material (atomic-number contrast).
All the NORM samples in this work were examined in a Camscan MX2500 scanning electron microscope that is fitted with an Oxford Instruments Ltd. “INCA Energy+” X-Max 80 Silicon drift detector for acquiring energy-dispersive X-ray (EDX) spectra. Back-scattered electron images, which show atomic number contrast were examined for the presence of impurity phases within the sampled materials. The Scanning Electron Microscope was operated at an accelerating voltage of 30 kV, and EDX spectra were measured over a time period of 300 seconds to allow detection of elements present in low concentrations i.e. ≈ 0.1 wt%. The NORM samples were attached to scanning electron microscope stubs using double-sided conductive carbon disks. A thin layer of carbon was deposited on to the samples by a thermal evaporation process to make them electrically conductive for electron microscopy and EDX analysis.

![Image of Camscan MX2500 scanning electron microscope]

Figure 4.9- Photograph of the Camscan MX2500 scanning electron microscope for the measurement of NORM materials at NPL.
4.6 Detection limits

The limit of detection (L_d) must be determined to evaluate the performance of the whole method for analysing a given radionuclide. In this work the L_d will be required for measurements carried out on: γ-ray spectrometry, ICP-MS and α-spectrometry, where the following parameters are considered (IAEA, 2010):

- counting time (of standards, blanks and sample)
- detector background and efficiency,
- the chemical yield or recovery,
- the analysed aliquot of the sample (mass or volume).

The traditional method was proposed by Currie (1968) and defines two values: the critical level or decision threshold, (L_c), as the level of the net signal below which the gross signal has no difference from the blank sample and the limit of detection (L_d) can be defined as the level at which the true net counts will be detected above the acceptable level in a given counting system (Currie, 1968).

It is given by the following expression (Curie, 1968)

\[
LLD = (4.653 \times \sigma_{N_B}) + 2.706 \hspace{1cm} (Equation \ 4.13)
\]

where \( \sigma_{N_B} \) is the standard deviation of counts in a blank (or de-ionized water) sample.

The standard deviation of the counts per unit time is determined by \( \frac{\sqrt{\text{Number of counts}}}{\text{Duration of measurement}} \).
The Minimum Detectable Activity (MDA) of a detector is an energy-specific measure of the activity required to identify a radiation source with an amount of statistical certainty (normally 95% or 2σ) (Knoll, 2010) assuming all above background. In some instances, such as in the regulation of NORM waste, it is required that a certain minimum detectable amount (MDA) of activity be measurable while monitoring for the possible presence of radioactive contaminants. One of the most widely used definitions of MDA was first introduced by Currie (Currie, 1968).

\[
MDA = \frac{4.653\sigma_{Nb} + 2.706}{p_{\gamma}E_{f}T} (Equation 4.14)
\]

where \(E_{f}\) is the full-energy peak, \(p_{\gamma}\) is the gamma emission probability and \(T\) is the counting time. The MDA per unit mass of a sample can be determined by rearranging the following equation:

\[
\frac{MDA}{m} = \frac{4.653\sigma_{Nb} + 2.706}{p_{\gamma}E_{f}T \times m} (Equation 4.15)
\]

where \(m\) is the mass of the sample.

However, the Currie formula does not define the width of the peak region (number of channels). The width defines the total counts and thus is very important in the determination of the MDA. ISO standard 11929-2010 is increasingly being used in measurement laboratories in many countries because it defines several important details of the detection limit calculations, especially for counting nuclear radiation (ISO 11929-2010; IAEA, 2010).
From ISO 11929-2010, the decision threshold should be calculated using the following formula:

\[
L_c = \frac{1}{w} \cdot k \cdot \sqrt{\frac{R_0}{t_{M,S}}} + \frac{R_0}{t_{M,0}} \quad (Bq \ L^{-1} Bq \ kg^{-1}) \quad (Equation \ 4.16)
\]

The detection limit can then be estimated using the expression:

\[
L_d = \frac{2 \cdot L_c + \frac{1}{t_{M,S}} k^2 w}{1 - k^2 \cdot s^2(w)} \quad (Bq \ L^{-1} Bq \ kg^{-1}) \quad (Equation \ 4.17)
\]

where \( R_0 \) is the background count rate (s\(^{-1}\)), \( k \) being the coverage factor, \( t_{M,S} \) the counting time of the sample and \( t_{M,0} \) is the counting of the background (s). The parameter \( w \) is determined using the following formula:

\[
w = \frac{1}{q_s \cdot \varepsilon \cdot N} \quad (Equation \ 4.18)
\]

where \( q_s \) is the sample quantity (mass (kg) or volume (\( V_s \))), \( \varepsilon \) is the counting efficiency, \( N \) is the chemical recovery of the radionuclide to be analysed and \( s(w) \) is the uncertainty of the factor \( w \).
Chapter 5

5. Measurement of Naturally Occurring Radioactivity Materials

5.1 General review of NORM

The Earth and its atmosphere contains many different Naturally Occurring Radioactive Materials (NORMs), which can be subdivided into two general categories; cosmogenic and terrestrial (Kathren, 1998) and all minerals and raw materials containing radionuclides of natural origin (UNSCEAR, 2000). The most significant radionuclides for the purposes of radiation protection are the radionuclides in the $^{238}$U, $^{232}$Th decay series and $^{40}$K (IAEA, 2011).

The high-Z, long-lived naturally occurring radioactive elements uranium and thorium and their decay products such as radium and radon are routinely present in the Earth's crust and atmosphere. As can be seen in Table 5.1 these heavy elements, along with $^{237}$Np (which is produced following the $\alpha$ decay of $^{241}$Am) head the four significant heavy element decay-chains, which can be labelled by mass numbers $4n$, $4n + 1$, $4n + 2$ and $4n + 3$, where $n$ is an integer.
<table>
<thead>
<tr>
<th>Name of Series</th>
<th>Type</th>
<th>Final Nucleus</th>
<th>Longest-Lived Member</th>
<th>Nucleus</th>
<th>Half-Life (y)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thorium</td>
<td>$4n$</td>
<td>$^{208}\text{Pb}$</td>
<td>$^{232}\text{Th}$</td>
<td>1.40 (1) $\times 10^{10}$</td>
<td>Browne, Nuclear Data Sheets 107, 2579 (2006)</td>
<td></td>
</tr>
<tr>
<td>Neptunium</td>
<td>$4n+1$</td>
<td>$^{209}\text{Bi}$</td>
<td>$^{237}\text{Np}$</td>
<td>2.144 (7) $\times 10^{6}$</td>
<td>Basunia, Nuclear Data Sheets 107, 2579 (2006)</td>
<td></td>
</tr>
<tr>
<td>Uranium</td>
<td>$4n+2$</td>
<td>$^{206}\text{Pb}$</td>
<td>$^{238}\text{U}$</td>
<td>4.468 (6) $\times 10^{9}$</td>
<td>Browne and Tuli, Nuclear Data Sheets 127, 191 (2015)</td>
<td></td>
</tr>
<tr>
<td>Actinium</td>
<td>$4n+3$</td>
<td>$^{207}\text{Pb}$</td>
<td>$^{235}\text{U}$</td>
<td>7.04 (1) $\times 10^{8}$</td>
<td>Browne and Tuli, Nuclear Data Sheets 122, 205 (2014)</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1- The $4n + x$ heavy element radioactive decay chains (ENSDF).

5.1.1 NORM of cosmogenic origin

Cosmogenic NORM is the result of interactions between the atomic nuclei of gases in the earth’s atmosphere and energetic cosmic rays. They are formed following the spallation of nuclei and neutron capture reactions in the atmosphere due to these cosmic bombardments (Klement, 1982). A list of the main cosmogenic radionuclides is shown in Table 5.2. They are in general light elements, with half-lives ranging from minutes to $7.17 \times 10^5$ (Kathren, 1998).
<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-Life</th>
<th>Decay-Mode and characteristic γ-ray energy</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>³H</td>
<td>12.32 (2) y</td>
<td>β⁻ (100%)</td>
<td>Tilley and Godwin, <em>et al.,</em> Nuclear Physics A708, 3 (2002)</td>
</tr>
<tr>
<td>⁷Be</td>
<td>53.22 (6) d</td>
<td>EC (100%) and γ (477 keV)</td>
<td>Tilley and Godwin, <em>et al.,</em> Nuclear Physics A708, 3 (2002)</td>
</tr>
<tr>
<td>¹⁰Be</td>
<td>1.51 × 10⁶ (4) y</td>
<td>β⁻ (100%)</td>
<td>Kelley and Godwin, <em>et al.,</em> Nuclear Physics A745, 155 (2005)</td>
</tr>
<tr>
<td>¹⁴C</td>
<td>5700 (30) y</td>
<td>β⁻ (100%)</td>
<td>Ajzenberg-Selove, Nuclear Physics A523,1 (1991)</td>
</tr>
<tr>
<td>²²Na</td>
<td>2.60 29 (8) y</td>
<td>β⁺ and γ (1275 keV)</td>
<td>Basunia, Nuclear Data Sheets 127, 69(2015)</td>
</tr>
<tr>
<td>²⁶Al</td>
<td>717 × 10³ (24) y</td>
<td>EC (100%)</td>
<td>Endt, <em>et al.,</em> Nuclear Physics A633, 1 (1998)</td>
</tr>
<tr>
<td>³²Si</td>
<td>153 (19) y</td>
<td>β⁻ (100%)</td>
<td>Ouellet and Singh., Nuclear Data Sheets 112, 2199 (2011)</td>
</tr>
<tr>
<td>³²P</td>
<td>14.268 (5) d</td>
<td>β⁻ (100%)</td>
<td>Ouellet and Singh., Nuclear Data Sheets 112, 2199 (2011)</td>
</tr>
<tr>
<td>³⁵S</td>
<td>87.37 (4) d</td>
<td>β⁻ (100%)</td>
<td>Ouellet and Singh., Nuclear Data Sheets 112, 2199 (2011)</td>
</tr>
<tr>
<td>³⁶Cl</td>
<td>3.013 × 10⁵ (15) y</td>
<td>EC (1.9%), β⁻ (98.1%)</td>
<td>Nica, Cameron and Singh, Nuclear Data sheets 113, 1 (2012)</td>
</tr>
<tr>
<td>³⁹Ar</td>
<td>269 (3) y</td>
<td>β⁻ (100%)</td>
<td>Nica, Cameron and Singh, Nuclear Data sheets 113, 1 (2012)</td>
</tr>
<tr>
<td>⁸¹Kr</td>
<td>2.29 × 10⁵ (11) y</td>
<td>EC (100%)</td>
<td>Baglin, Nuclear Data Sheets 109, 2257 (2008)</td>
</tr>
</tbody>
</table>

Table 5.2- Principal cosmogenic radionuclides produced in the Earth’s atmosphere.

### 5.1.2 NORM of terrestrial Origin

Terrestrial radionuclides, also known as primordial radionuclides, refer to radioactive materials that have been on the earth since its formation (Klement, 1982). These can be further split into two sub-groups, single decaying nuclei (Table 5.3) and those comprised of the three main
radioactive decay series, (Table 5.1). According to Kathren, (1998) over twenty naturally occurring single primordial isotopes exist; most are β emitters, with half-lives greater than $10^{10}$ years. From a metrological standpoint supporting the current work, of the singly occurring primordial radionuclides only $^{40}$K (Figure 5.1) is of significance. Decaying to both $^{40}$Ca and $^{40}$Ar, it has a half-life of $1.28 \times 10^9$ years and emits a characteristic photon with an energy of 1.461 MeV which corresponds to the $2^+ \rightarrow 0^+ \gamma$ ray decay in the $^{40}$Ar daughter nucleus; this is the signature used for identifying $^{40}$K by γ-ray spectrometry (Cameron and Singh, 2004).

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-life (y)</th>
<th>Decay mode and characteristic main γ energy (keV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{40}$K→$^{40}$Ar $^{40}$Ca</td>
<td>$1.28 (3) \times 10^9$ y</td>
<td>β (89.28%) EC (10.72%) → γ ray decay 1460.8</td>
<td>Singh. Nuclear Data Sheets 102, 293 (2004)</td>
</tr>
<tr>
<td>$^{87}$Rb→$^{87}$Sr</td>
<td>$4.81 (9) \times 10^{10}$ y</td>
<td>β (100%) (no γ ray decays)</td>
<td>Johnson and Kulp, Nuclear Data Sheets 129, 1 (2015)</td>
</tr>
<tr>
<td>$^{113}$Cd→$^{113}$I</td>
<td>$9 (5) \times 10^{15}$ y</td>
<td>β and→ γ ray 263.7</td>
<td>Blachot, Nuclear Data Sheets 111, 1471 (2010)</td>
</tr>
<tr>
<td>$^{138}$La→$^{138}$Ba</td>
<td>$1.02 (1) \times 10^{11}$ y</td>
<td>β (34.8%); EC (65.2%)→ γ ray 788.7, 1435.8</td>
<td>Sonzogni., Nuclear Data Sheets 98, 515 (2003)</td>
</tr>
<tr>
<td>$^{176}$Lu→$^{176}$Yb</td>
<td>$3.6 (2) \times 10^{10}$ y</td>
<td>β (100%)→ γ ray 88.34, 201.83, 306.78</td>
<td>Basunia, Nuclear Data Sheets 107, 2579 (2006)</td>
</tr>
<tr>
<td>$^{187}$Re→$^{187}$Os</td>
<td>$5 \times 10^{10}$ h</td>
<td>β (100%)→ no γ ray decays</td>
<td>Basunia, Nuclear Data Sheets 110, 999 (2009)</td>
</tr>
</tbody>
</table>

Table 5.3- Selected single decay primordial radionuclides.
5.2 NORM decay Series

The long lived primordial decay nuclei $^{238}$U, $^{235}$U and $^{232}$Th, all have half-lives that are of the order of the age of the earth and decay by a series of $\alpha$ and $\beta$ emission, with decreasing $Z$ and $A$ until a lighter, stable Pb nucleus is reached. Some of these decay sequences populate excited states in their respective radioactive daughter nuclei and de-excite via $\gamma$-ray emission.

4n Thorium series

The 4n Thorium series is approximately four times more abundant than uranium in the Earth’s crust (Ashley, et al, 2012). $^{232}$Th is commonly found in high concentration in monazite sand samples (Tillu, 1954). The 4n Thorium series predominantly undergoes $\alpha$ decay, thus making measurement via $\alpha$-particle spectrometry significant. The activity of $^{232}$Th chain can be inferred...
by γ-ray spectrometry of the decay daughters in a given sample under the assumption of secular equilibrium.

4n + 2 Uranium series

Naturally occurring uranium is formed of three isotopes $^{238}\text{U}$, $^{235}\text{U}$ and $^{234}\text{U}$, of which 99.27% is made up of $^{238}\text{U}$ (Kathren, 1998). $^{238}\text{U}$ and $^{234}\text{U}$ are part of the 4n + 2 Uranium series, whereas $^{235}\text{U}$ (0.72% abundance) heads the 4n + 3 Actinium series. The 4n + 2 series terminates at $^{206}\text{Pb}$, (Table 5.4). Due to its daughters having shorter half-lives than the parent $^{238}\text{U}$, secular equilibrium can result for the decay series members. Thus by measuring samples containing members of the uranium decay series by high resolution γ-ray spectrometry, the activity concentration of $^{238}\text{U}$ can be determined (Malain, et al, 2012), under the assumption of no chemical fractionation and secular equilibrium.

4n + 3 Actinium series

$^{235}\text{U}$ is fissile, makes up approximately 0.72% of all natural uranium (Kathren, 1998), and is used as the primary fission nuclear fuel. It heads the 4n + 3 Actinium series which decays ultimately to $^{207}\text{Pb}$. The decay chain members of $^{235}\text{U}$ can be measured by both α-spectrometry and γ-ray spectrometry. Direct measurement of $^{235}\text{U}$ by γ-ray spectrometry can however be complicated by the presence of a doublet characteristic γ ray at 186 keV which arises both from the α decay of $^{235}\text{U}\rightarrow^{231}\text{Th}$ and also following the α decay of $^{226}\text{Ra}$ in the uranium (4n+2) decay chain. Alpha-spectrometry can also be utilised for activity concentration measurements of members of the $^{235}\text{U}$ decay chain (Crespo, 2012).
<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life</th>
<th>Decay mode</th>
<th>Main characteristic α-decay energy (keV)</th>
<th>Main characteristic γ-ray energy (keV)</th>
<th>γ Emission Probability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{232}$Th</td>
<td>1.405 (6) × 10$^{10}$ y</td>
<td>α</td>
<td>4 011.2 (14)</td>
<td>63.81 (2)</td>
<td>0.263 (13)</td>
</tr>
<tr>
<td>$^{228}$Ra</td>
<td>5.75 (3) y</td>
<td>β-</td>
<td>-</td>
<td>13.52 (2)</td>
<td>-</td>
</tr>
<tr>
<td>$^{228}$Ac</td>
<td>6.15 (2) h</td>
<td>β-</td>
<td>-</td>
<td>911.204 (4)</td>
<td>25.8 (4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>968.971 (17)</td>
<td>15.8 (3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>338.320 (3)</td>
<td>11.27 (12)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>964.766 (10)</td>
<td>4.99 (9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>463.004 (6)</td>
<td>4.40 (7)</td>
</tr>
<tr>
<td>$^{228}$Th</td>
<td>1.9116 (16) y</td>
<td>α</td>
<td>5 423.24 (22)</td>
<td>84.373 (3)</td>
<td>1.22 (2)</td>
</tr>
<tr>
<td>$^{224}$Ra</td>
<td>3.66 (4) d</td>
<td>α</td>
<td>5 685.48 (15)</td>
<td>240.986 (6)</td>
<td>4.10 (5)</td>
</tr>
<tr>
<td>$^{222}$Rn</td>
<td>55.6 (1) s</td>
<td>α</td>
<td>6 288.22 (10)</td>
<td>549.76 (4)</td>
<td>0.114 (17)</td>
</tr>
<tr>
<td>$^{216}$Po</td>
<td>0.145 (2) s</td>
<td>α</td>
<td>6 778.4 (5)</td>
<td>804.9 (5)</td>
<td>0.0019 (3)</td>
</tr>
<tr>
<td>$^{212}$Pb</td>
<td>10.64 (1) h</td>
<td>β-</td>
<td>-</td>
<td>238.632 (2)</td>
<td>43.3 (3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>300.087 (10)</td>
<td>3.28 (3)</td>
</tr>
<tr>
<td>$^{212}$Bi</td>
<td>60.55 (6) m</td>
<td>α</td>
<td>6 051.04 (3)</td>
<td>727.330 (9)</td>
<td>6.58 (6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(35.93%)</td>
<td></td>
<td>1620.50 (10)</td>
<td>1.49 (4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(64.07%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{212}$Po</td>
<td>0.299 (2) μs</td>
<td>α</td>
<td>8 785.17 (11)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$^{208}$Tl</td>
<td>3.053 (4) m</td>
<td>β-</td>
<td>-</td>
<td>2614.533 (13)</td>
<td>35.64 (6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>583.191 (2)</td>
<td>30.4 (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>510.77 (10)</td>
<td>8.13 (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>860.564 (5)</td>
<td>4.47 (4)</td>
</tr>
<tr>
<td>$^{206}$Pb</td>
<td>Stable</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.4- Characteristic decay details for the 4n Thorium decay series (data taken from DDEP).
Figure 5.2- Schematic of the 4n Thorium decay series.

Figure 5.3- Schematic of the 4n + 2 Uranium decay series.
<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life</th>
<th>Decay mode</th>
<th>Main characteristic α-decay energy (keV)</th>
<th>Main characteristic γ-ray energy (keV)</th>
<th>γ Emission Probability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>238U</td>
<td>$4.468 \times 10^9$ y</td>
<td>α</td>
<td>4 198 (3)</td>
<td>49.55 (6)</td>
<td>0.063 (7)</td>
</tr>
<tr>
<td>232Th</td>
<td>24.10 (3) d</td>
<td>β−</td>
<td>-</td>
<td>63.283 (6)</td>
<td>4.1 (7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>92.370 (10)</td>
<td>2.42 (15)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>92.793 (10)</td>
<td>2.39 (15)</td>
</tr>
<tr>
<td>234mPa</td>
<td>1.17 (3) m</td>
<td>β−</td>
<td>-</td>
<td>1001.03 (3)</td>
<td>0.837 (10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>766.38 (2)</td>
<td>0.294 (12)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>742.81 (3)</td>
<td>0.080 (4)</td>
</tr>
<tr>
<td>234U</td>
<td>$2.455 \times 10^5$ y</td>
<td>α</td>
<td>4 775 (7)</td>
<td>53.20 (2)</td>
<td>0.123 (2)</td>
</tr>
<tr>
<td>230Th</td>
<td>75380 (30) y</td>
<td>α</td>
<td>4 687 (15)</td>
<td>67.672 (2)</td>
<td>0.373 (21)</td>
</tr>
<tr>
<td>226Ra</td>
<td>1600 (7) y</td>
<td>α</td>
<td>4 601 (7)</td>
<td>186.211 (13)</td>
<td>3.59 (6)</td>
</tr>
<tr>
<td>222Rn</td>
<td>3.8235 (3) d</td>
<td>α</td>
<td>5 489 (30)</td>
<td>511 (2)</td>
<td>0.076</td>
</tr>
<tr>
<td>218Po</td>
<td>3.10 (1) m</td>
<td>α</td>
<td>(99.978 %) , β− (0.0022 %)</td>
<td>6 002 (9)</td>
<td>-</td>
</tr>
<tr>
<td>214Pb</td>
<td>26.8 (9) m</td>
<td>β−</td>
<td>-</td>
<td>351.932 (2)</td>
<td>35.1 (4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>295.224 (2)</td>
<td>18.2 (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>241.997 (3)</td>
<td>7.12 (11)</td>
</tr>
<tr>
<td>218At</td>
<td>1.6 s</td>
<td>α</td>
<td>6 694 (3)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>214Bi</td>
<td>19.9 (4) m</td>
<td>α</td>
<td>(0.021%) , β− (99.979 %)</td>
<td>5 452 (3)</td>
<td>44.6 (5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1764.494 (14)</td>
<td>15.1 (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1120.287 (10)</td>
<td>14.7 (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1238.110 (12)</td>
<td>5.78 (8)</td>
</tr>
<tr>
<td>214Po</td>
<td>164.3 (20) μs</td>
<td>α</td>
<td>7 687 (6)</td>
<td>799.7 (1)</td>
<td>0.0104 (35)</td>
</tr>
<tr>
<td>210Tl</td>
<td>1.3 m</td>
<td>β−</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>210Pb</td>
<td>22.3 (2) y</td>
<td>β−</td>
<td>-</td>
<td>46.539 (1)</td>
<td>4.25 (4)</td>
</tr>
<tr>
<td>210Bi</td>
<td>5.013 (5) d</td>
<td>α</td>
<td>(0.00014 %) , β− (99.9998 %)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>210Po</td>
<td>138.376 (2) d</td>
<td>α</td>
<td>5 304 (7)</td>
<td>803.10 (5)</td>
<td>0.00122 (4)</td>
</tr>
<tr>
<td>206Pb</td>
<td>Stable</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.5- Characteristic decay details for the $4n + 2$ Uranium series (data taken from DDEP).
<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life</th>
<th>Decay mode</th>
<th>Main characteristic $\alpha$-decay energy (keV)</th>
<th>Main characteristic $\gamma$-ray energy (keV)</th>
<th>$\gamma$ Emission Probability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{235}$U</td>
<td>$7.038 \times 10^8$ y</td>
<td>$\alpha$</td>
<td>$4398$ (13)</td>
<td>$185.715$ (5)</td>
<td>$143.764$ (2)</td>
</tr>
<tr>
<td>$^{231}$Th</td>
<td>$25.52$ (1) h</td>
<td>$\beta^-$</td>
<td>-</td>
<td>$25.646$ (4)</td>
<td>$84.216$ (3)</td>
</tr>
<tr>
<td>$^{231}$Pa</td>
<td>$3.276 \times 10^5$ y</td>
<td>$\alpha$</td>
<td>$5015$ (8)</td>
<td>$27.36$ (1)</td>
<td>$300.07$ (1)</td>
</tr>
<tr>
<td>$^{227}$Ac</td>
<td>$21.773$ (3) y</td>
<td>$\alpha$ (1.38%), $\beta^-$ (98.62%)</td>
<td>$4953$ (14)</td>
<td>$99.6$ (1)</td>
<td>$0.0056$ (17)</td>
</tr>
<tr>
<td>$^{227}$Th</td>
<td>$18.72$ (2) d</td>
<td>$\alpha$</td>
<td>$5757$ (15)</td>
<td>$235.971$ (20)</td>
<td>$50.13$ (1)</td>
</tr>
<tr>
<td>$^{223}$Ra</td>
<td>$11.435$ (4) d</td>
<td>$\alpha$</td>
<td>$5534$ (15)</td>
<td>$269.459$ (10)</td>
<td>$154.21$ (1)</td>
</tr>
<tr>
<td>$^{219}$Rn</td>
<td>$3.96$ (1) s</td>
<td>$\alpha$</td>
<td>$6819$ (3)</td>
<td>$271.23$ (1)</td>
<td>$401.81$ (41)</td>
</tr>
<tr>
<td>$^{211}$Po</td>
<td>$1.781$ (4) ms</td>
<td>$\alpha$</td>
<td>$7386$ (8)</td>
<td>$438.8$ (3)</td>
<td>$401.81$ (41)</td>
</tr>
<tr>
<td>$^{211}$Pb</td>
<td>$36.1$ (2) m</td>
<td>$\beta^-$</td>
<td>-</td>
<td>$404.853$ (10)</td>
<td>$832.01$ (3)</td>
</tr>
<tr>
<td>$^{211}$Bi</td>
<td>$2.14$ (2) m</td>
<td>$\alpha$ (99.724 %), $\beta^-$ (0.276%)</td>
<td>$6622$ (6)</td>
<td>$351.059$ (20)</td>
<td>$12.91$ (11)</td>
</tr>
<tr>
<td>$^{211}$Po</td>
<td>$0.516$ (3) s</td>
<td>$\alpha$</td>
<td>$7450$ (3)</td>
<td>$897.80$ (5)</td>
<td>$569.70$ (22)</td>
</tr>
<tr>
<td>$^{209}$TI</td>
<td>$4.77$ (2) m</td>
<td>$\beta^-$</td>
<td>-</td>
<td>$897.80$ (5)</td>
<td>$0.260$ (9)</td>
</tr>
<tr>
<td>$^{209}$Pb</td>
<td>Stable</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.6- Characteristic decay details for the $4n + 3$ Actinium series (data taken from DDEP).
Figure 5.4- Schematic of the 4n + 3 Actinium series headed by $^{235}$U.

5.3 NORM Radionuclides of interest in this study

The characteristics of the following radionuclides, as given in Tables 5.4, 5.5 and 5.6 were measured as part of the design and production of the NORM reference materials by $\gamma$-ray spectrometry. The activities of some long half-life radionuclides were based on the measurements of their short-lived daughters. This is the case for:
- $^{238}\text{U}$, measured activity of $^{238}\text{U}$ decay by $\alpha$-decay to $^{234}\text{Th}$
- $^{226}\text{Ra}$, measured from the $\alpha$-decay and $\beta^-$ decay $\gamma$ rays follows the decays of $^{214}\text{Pb}$ and $^{214}\text{Bi}$, assuming secular equilibrium with $^{226}\text{Ra}$
- $^{210}\text{Pb}$ measured directly via 47 keV line, from the $\gamma$ ray of $^{210}\text{Pb} \rightarrow ^{210}\text{Pb} \beta^-$ decay
- $^{228}\text{Ra}$, measured via the $\gamma$-ray decay transitions associated with $^{228}\text{Ac} \beta^-$ decay
- $^{228}\text{Th}$, measured using $\gamma$-ray emissions following the radioactive decays of $^{224}\text{Ra}$, $^{212}\text{Pb}$, $^{212}\text{Bi}$ and $^{208}\text{Tl}$
- $^{235}\text{U}$, measured directly via 185.7 $\gamma$ line, which is corrected for the $^{214}\text{Bi}$ and $^{214}\text{Pb}$ decay activity concentrations in the $^{226}\text{Ra}$ decay chain

Alpha-Spectrometry and ICP-MS techniques were used to measure the following radionuclides directly:

- $^{238}\text{U}$, $^{234}\text{U}$ ($\alpha$-spectrometry and ICP-MS measurement)
- $^{232}\text{Th}$, $^{230}\text{Th}$ and $^{228}\text{Th}$ ($\alpha$-spectrometry and ICP-MS measurement)
- $^{210}\text{Po}$ ($\alpha$-spectrometry)

From the $4n$ Thorium series and $4n + 2$ Uranium series, the measurements focused on the decays of natural thorium and uranium (UNSCEAR, 2000). Thorium is also present as $^{230}\text{Th}$ and $^{227}\text{Th}$ in the $4n + 2$ and $4n + 3$ chains respectively, but $^{232}\text{Th}$ is virtually 100% of NORM thorium found in nature by weight (Kathren, 1998).

Radium rich waste products such as phosphogypsum and wastes attributed to TiO$_2$ have been found to show elevated levels of both Pb and Po (Mathews, et al, 2007). Both $^{210}\text{Pb}$ and $^{210}\text{Po}$
are particle reactive and are rapidly removed from the water column by adsorption onto sinking particulates or they may be co-precipitated with ferric hydroxides and manganese oxides (Mathews, et al, 2007). Due to different chemical properties of the isotopes, they are often in disequilibria. In solution both isotopes cannot be assumed to be in radioactive equilibrium with each other and therefore it is important to be able to determine both separately.

Another member of the $4n + 2$ Uranium series, $^{226}$Ra is of particular significance as a source of (TE)NORM (UNSCEAR, 2000). The isotope is used in a variety of commercial, industrial and medical activities (Kathren, 1998). $^{226}$Ra decays to $^{222}$Rn, which along with $^{220}$Rn, from the $4n$ series, is the source of much of the heavy-element radioactivity found in the atmosphere. Radium is also significant in the $4n$ Thorium series, via $^{228}$Ra. Since radium is a Group 2 element (along with calcium), due to its solubility (Kathren, 1998), radium can leach from soils and form compounds that can be taken up by plants and animals, in a way analogous to calcium.

The $4n + 3$ chain measurements focus on the direct measurement of $^{235}$U via α-decay, although not measured in this EngD thesis $^{223}$Ra is also of current interest as an α emitting radiopharmaceutical for cancer therapy (Keightley, et al, 2015; Collins, et al, 2015).

5.4 NORM reference materials as part of MetroNORM

As part of the project the following candidate materials were analysed by NPL:

- Coal ash (mining and combustion industries, (Mishra, 2004))
- TiO$_2$ waste/residues (paint pigment, (Gázquez, et al, 2012))
- Tuff (building industry in Italy, (Maringer, et al, 2013))
- Sludge (MnO$_2$) (fracking and waste water industry, (Pahola, 2015))
- Sandy oil mixture (oil and gas industry, (Garner, 2015))

Each material was assayed by $\gamma$-ray spectrometry and $\alpha$-spectrometry following radiochemical separation. Based on the availability and activity concentration from the initial measurements carried out, the final three candidate reference materials selected for use in the project were:

- TiO$_2$ waste/residues,
- Tuff,
- Sandy oil mixture.

### 5.4.1 TiO$_2$ waste

Titanium dioxide is a simple inorganic compound commercially produced as a white powder. It is commonly available in two main crystal forms, ilmenite and rutile (IAEA, 2011) and typically supplied to the market in a range of package sizes or in bulk. The material is used as a white pigment in paints and plastics, although none of the NORM activity transfers to the Titanium Dioxide products (Garcia-Tenorio, et al, 2013). The majority of the input activity transfers to process wastes which need to be managed properly, prior to disposal. Processing of TiO$_2$ bearing raw materials may generate scale deposits and other wastes that may contain increased radionuclide levels. The material obtained in this study is from a TiO$_2$ processing facility in Prague, Czech Republic, which supplied NPL with 10 kg of un-dissolved raw material waste from processing that had been carried out in 2014.
5.4.2 Tuff

Tuff (from the Italian tufo) is a type of rock made of volcanic ash ejected from a vent during a volcanic eruption which is used as a building material in Italy. In the ancient world, Tuff's relative softness meant that it was commonly used for construction where available. The material used in this work is called ‘bianco a scaglie nere’ and is typical of the Sabatini Mountains located to the north of Rome. NPL were sent 5 kg block of Tuff by an Italy cement firm, to do analysis on the material.

5.4.3 Sandy Oil

The Sand samples used in the project originated from the petroleum exploration industry in Kuwait, and were sampled from the vicinity of oilfields. The oil logging process can lead to shale formations being disrupted, leading to the release of NORM isotopes to the surface during oil/gas drilling operations (Escott, 1984). The samples were selected from a variety of locations to ensure accurate representation of the distribution of the NORM materials in the environment. The removal and collection of the soil was carried out using a shovel, where a sample was taken at depths of 5-25 cm covering around 15 cm diameter on the surface, the sample was then placed in a large container sealed and numbered.

5.5 Experimental methodology of NORM reference materials

5.5.1 Sample preparation of NORM reference materials

Once the Tuff, TiO$_2$ and Sand samples were received from Italy, Czech Republic and Qatar respectively, the samples were prepared for measurements in the NPL Environmental laboratory (Harms and Gilligan, 2012).
5.5.1.1 Tuff

The Tuff was sent as a brick, which was approximately 10 kg, it was crushed coarsely in a fume cupboard using a hammer with the aim of obtaining particles of Tuff small enough to be inserted into a grinder (Figure 5.5). Once crushed into smaller pieces the material was ground coarsely in a jaw crushe at a distance of 10 mm. The powdered Tuff was inserted into an oven at a temperature of 120 °C for about 24 hours to eliminate any moisture present in the sample. The optimum drying time was estimated by weighing the sample every three hours until a constant weight was observed for at least three successive measurements. The drying of the sample carried out during the grinding process enabled the ratio of original mass to dry mass (1.13) to be calculated.

![Figure 5.5- Photograph of the Tuff brick before crushing. A cigarette lighter is shown in the foreground for scale.](image)

The Tuff was then ground a second time by setting the jaws of the grinder to the shortest distance possible. Once the grinding was completed the material was then sieved using a 150
µm sieve and was performed to produce uniform and homogeneous samples of Tuff and Sand. The contents were then transferred into an Inversina two litre mixer and mixed for 24 hours. After which 100 grams of both were then bottled into four separate 125 mL Azlon bottles. Three of these were used for direct measurement using γ-ray spectrometry and were sealed with PVC tape. They were then stored for at least one month in order to allow for secular equilibrium of $^{222}\text{Rn}$ with its parent $^{226}\text{Ra}$. The other bottle was used for radiochemical analysis and to prepare samples for alpha and ICP-MS measurements.

5.5.5.2 Sand

The Sand was initially sieved with a 1 mm sieve to ensure that all the excess impurities such as vegetation and larger particulates were removed. Once sieved, the samples were dried using the NPL microwave oven to remove excess moisture, where the sand sample was dried at 50°C for 24 hours to ensure a constant weight of sample. The methodology was based on the procedure carried out on the Tuff material.

5.5.5.3 Titanium dioxide

The TiO$_2$ material preparation was a much more complex sample preparation. The raw material arrived at NPL in bottles which had a significant moisture content. In order to standardise the material, the contents were removed from the bottle and transferred into several large beakers for drying in a microwave for an initial 24 hours at 180°C and then a further 24 hours at 120°C to remove most of the moisture content. Once dry the material was transferred from microwave oven into a mortar and carefully crushed, to reduce the size of particles further, once the material was crushed in a mortar the contents was then ground into powder form using a gyro-mill.
The contents were then sieved to 150 µm (100 mesh) and the material was then transferred into an Inversina two litre mixer, to produce a homogenised powder after which the material was bottled into a 500 gram Azlon bottle. In common with the Sand and Tuff samples, three samples were bottled into 125 mL Azlon bottles, two of which were sealed with PVC tape for γ-ray spectrometry and one for radiochemical analysis.

5.6 Radiochemical Analysis

5.6.1 Sample preparation of sources for α and ICP-MS measurement

The reference materials are solid complex matrices that must be dissolved in order to perform radiochemical techniques to isolate the nuclides of interest. Prior to sample digestion the matrices were spiked with 10 Bq of NPL certificated radioactive tracers $^{236}$U and $^{229}$Th (Figure 5.7; certificates in Appendix F) with the purpose to use them as yield and counting efficiency tracers. They were picked due to them having a clear, discrete signature energy that would not interfere with the measurement of $^{238/234}$U and $^{232/230/228}$Th. A commonly used uranium tracer is $^{232}$U, however this tracer is unsuitable for ICP-MS due to its half-life ($T_{1/2} = 68.9$ years).
(Basunia, 2006) and α-spectrometry as $^{232}$U daughter $^{228}$Th peak energies interfere with measurements, due it being part of the NORM $4n$ Thorium decay chain.

Figure 5.7- Schematic of the decay series of the $^{229}$Th tracer.

Once spiked, the samples underwent dissolution through sample fusion, in order to be in a state to undergo radiochemical procedures via extraction chromatography. A process flow chart to demonstrate the procedures used is shown in Figure 5.8.
In order to work with these systems, it was necessary both to dissolve the reference material samples completely in order to eliminate any interfering elemental components in the measurement and keep the total sample volume for separation as low as possible. In the case of mineral matrices such as Sand, Tuff and TiO$_2$, silicates need to be adequately dissolved in order to assure dissolution of the radionuclides incorporated inside the silicate crystal structure of soils (such as natural uranium/thorium) (Croudace, et al, 1998). It was also necessary to
eliminate it from the matrix before starting the radiochemical analysis, as silica-monomers may transform into insoluble polymeric colloids or even precipitates. As a result of the literature review conducted in Chapter 3, the sample dissolution technique chosen for the analysis of Sand, Tuff and TiO₂ was fusion. Six sub-samples of each material were fused, along with a procedural blank, made of blank sand material, which has previously been used in NPL Environment Proficiency Test Exercises (Harms and Gilligan, 2012). A Katanax K2 Prime (Figure 5.9) was used for the fusion of samples to aid complete dissolution.

![Figure 5.9- Summary of procedure using the Katanax K2 system (Katanax, Canada).](image)

The samples were digested using an automated borate fusion technique using the Katanax K2, utilising a technique originally developed for concrete in a European Metrology Research Programme (EMRP) titled *Metrology for Radioactive Waste Management*. 0.5 g of each sample was added to a Pt crucible, along with 3 g lithium metaborate, 1.5 g lithium tetraborate, 0.25 g lithium bromide and 0.01 g lithium fluoride. The furnace was ramped up to 1,000°C, and the sample did not enter the Katanax until this temperature was reached. The samples were
fused at this temperature for 10 minutes. The temperature then ramped to 1,020°C and held for 1 minute. Throughout the procedure the Pt crucibles were rocked to aid the fusion. At the end of the procedure, the crucibles were tipped into PTFE beakers containing 50 mL of Milli-Q water (Millipore, USA) and acidified with 50 mL 20% (v/v) HNO₃ and stirred with a PTFE magnetic stirrer (Labortechnik, Germany). The crucible was rinsed carefully to digest any residual melt retained in the crucible, although losses of material throughout the process were kept to a minimum, this was not as significant an issue, due to the use of internal isotopic standards. The material was then placed onto a hot plate with a magnetic stirrer (Labortechnik, Germany) and evaporated down to around 30 mL of solution. Unavoidably, considerable amounts of boric acid and silica gel (dependent on the material) are present in the digestion cake which precipitate from acidic solutions and lead to coagulation of the samples. This has to be removed prior to chemical separation (Figure 5.10) (Crowdace, et al, 1998) as the samples will not flow through the extraction chromatography cartridges. The coagulation can be assisted by a flocculating agent (e.g. polyethylene glycol (PEG)) (PEG-2000, mol. wt. 2000; Aldrich Chemicals, Dorset, UK) supporting the precipitation of colloidal silica gel. (Crowdace, et al, 1998).

Figure 5.10- Photograph showing the samples forming a silica gel after Katanax fusion.
2 mL of 0.2 M PEG, to each digestion mixture prior to the digestion of the material, and after a six-hour period the material was vacuum filtering through a Whatman filter No. 540, which supported a Whatman GF-C filter paper. The filter papers were rinsed with 8 M HNO₃ and effectively retained the precipitate resulting in a clear solution being collected and to discard any residue polymerised silicates (Reading, et al, 2015). The solutions were then evaporated to dryness and re-dissolved in 10 mL of 3 M HNO₃ and subsequently taken for radiochemical separation.

5.6.1.1 Sample preparation of sources for a measurement of Po

A key factor in the preparation and analysis of samples for $^{210}$Po is the caution required to avoid losses due to volatilisation (Mathews, 2007). Thus, the sample preparation procedure did not use the Katanax method outlined above, fusion techniques from various studies showed substantial losses of polonium (Akbar, Hutton, & Prescott, 1985; Lowson & Short, 1986). Even with dry ashing, loss of polonium may occur at temperatures as low as 100 °C, with all polonium lost as the temperature approaches 800 °C (Cleary and Hamilton, 1968). Clearly, temperatures should be kept as low as the chosen procedure permits, however it has also been found that HNO₃ digestion alone has soon shown incomplete $^{210}$Po extraction (Card and Bell, 2005). The procedure followed was used by Vreček, et al, (2004) where samples were digested in Teflon beakers under prolonged acid leaching, rather than total dissolution. However previous work has also shown that experiments performed with HNO₃ digestion alone have shown incomplete $^{210}$Po extraction, when compared with the total dissolution methods (Card and Bell, 1985; Mathews, 2007).

Thus, in order to trace chemical losses during the analysis, as with the method outlined for Th and U isotopes, a key yield tracer is used. Two sets of each of the reference materials were
spiked with 10 Bq of NPL certificated standard of $^{209}$Po, along with a procedural blank, which again was the same sand material used in the uranium and thorium analysis. It must be noted there was an option to use $^{208}$Po, however due to their respective peak energies for $^{209}$Po 4,883 / 4,885 keV and $^{208}$Po 5,115 (Kondev, 2008), $^{209}$Po offered the better energy separation for $^{210}$Po. Cold leaching of the sample took place for 3 days as per Vrećek, et al, (2004) with concentrated hydrofluoric and nitric acid with a 4:1 ratio and then filtered, then cautiously evaporated to dryness and dissolved in 2 M HCL, for chemical separation.

5.6.2 Radiochemical separation UTEVA extraction of uranium and thorium isotopes

For both α-spectrometry and ICP-MS measurements it is critical that the spectra are free from thorium in the uranium spectra and vice versa. This is of particular importance for NORM measurements using α-spectrometry where the $4n$ Thorium series and $4n + 2$ Uranium series dominate with interfering alphas in a measurement which make it difficult to identify and quantify the various isotopes in the spectra due to peak overlap. This is as a result of improper radiochemical separation, this inevitability degrades the alpha-peak shape and limit achievable resolution (Horwitz, et al, 1992).

Following the method described by EICHROM Industries Inc. (2005), and adapted by Casacuberta, et al, (2012), the UTEVA resin columns (UT-C50-A) consisting of a 2 mL pre packed column, 100–150 µm particle size resin were opened and placed in a column rack, where the resin was allowed to drain and then preconditioned with 10 mL of 3 M HNO$_3$. With the reference material fractions being loaded onto the resin column with 5 mL of 3 M HNO$_3$. The column was then rinsed with 10 mL of 3 M HNO$_3$, where the eluted solutions were discarded to waste, while the U and Th were sorbed onto the resin. After converting the resin to chloride form with 9 M HCl (5 mL), thorium was stripped by passing 25 mL of a 5 M HCl-
0.05 M oxalic acid solution through the resin. Thorium was sufficiently purified in the elute of this fraction to be electroplated. The final step was the uranium elution with 15 mL of 0.01 M HCl (Figure 5.11).

The experiment was also performed in two replicates of each NORM sample to improve the precision of the analysis (Croudace, et al, 1998), as well as a procedural blank that was spiked with the same amount of yield tracer, with the aim to prove whether the sample matrix may influence the elution of the Th and U in the cleaning step.
Figure 5.11- Radiochemical separation of U and Th in UTEVA (EICHROM Industries Inc., 2005).
The separated Th and U fractions are measured by α-particle spectrometry and inductively coupled plasma triple quadrupole mass spectrometry (ICP-QQQ-MS), dividing each sample material into two aliquots:

a. 10 mL for alpha spectrometry
b. 1 mL for ICP-QQQ-MS

5.6.3 Po extraction using Sr resin

The chemical separation method used was based on the IAEA method (IAEA, 2012) developed for MetroNORM; the validated NPL procedure is also used for all of NPL customer work in relation to the standardisation of Po isotopes with A = 208, 209 and 210. Using the Sr resin for Po separation has shown chemical recoveries of around 70% (Vajda, et al, 1997). The pre-packed column was pre-conditioned with 50 mL of 2 M HCl, the 2 M HCl loading solution was then passed through the column and the non-retained ions were removed from the column with 90 mL 2 M HCl. In this fraction, Bi was also present. Then polonium was stripped with 60 mL 6 M HNO₃. After the polonium-loading solution was evaporated at a low temperature (<80 °C) to dryness, 1 mL of 2 M HCl was added to dissolve the residue. Then 100 mL of distilled water was added to the solution and transferred to a beaker to perform spontaneous deposition of Po radioisotopes for α-spectrometry (Vajda, et al, 1997; Vreček, et al, 2004; Miura, et al, 2000, Biggin, et al, 2002).

The experiment was also performed in two replicates of each NORM sample in order to improve the precision of the analysis (Croudace, et al, 1998), as well as a procedural blank that was spiked with the same amount of yield tracer, with the aim to prove whether the sample matrix may influence the elution of the Po in the cleaning step.
5.7 Instrumentation

5.7.1 Gamma-ray spectrometry

Gamma-ray spectrometry analysis of the NORM samples was carried out using a semi-planar detector ‘Lancelot’ (Harms and Gilligan, 2012) with a carbon fibre detector window was used to measure the NORM materials contained in the 125 mL Azlon bottles.

<table>
<thead>
<tr>
<th>Detector model</th>
<th>GEM-FX8530</th>
</tr>
</thead>
<tbody>
<tr>
<td>Serial number</td>
<td>49-P50541A</td>
</tr>
<tr>
<td>Diameter</td>
<td>85.1 mm</td>
</tr>
<tr>
<td>Length</td>
<td>33.2 mm</td>
</tr>
<tr>
<td>End cap to detector</td>
<td>5 mm</td>
</tr>
<tr>
<td>Carbon fibre</td>
<td>0.76 mm</td>
</tr>
<tr>
<td>Bias Voltage (V dc)</td>
<td>+ 3600</td>
</tr>
</tbody>
</table>

Table 5.7- Operational characteristics of the ‘Lancelot’ HPGe detector.

![Cross section of 'Lancelot' HPGe detector](image)

Figure 5.12- Cross section of ‘Lancelot’ HPGe detector (figure taken from ORTEC user manual for detector serial number 49-P50541A).
To reduce the external $\gamma$-ray background in the measured spectrum, a cylindrical lead shield with a fixed bottom and a movable cover shields the detector. The HPGe detector is designed for low background measurements. It sits inside a low-background lead shield consisting of an outer layer of 11 cm ‘contemporary’ lead at 500 Bq kg$^{-1}$ $^{210}$Pb and an inner layer of 9 cm ‘old’ 16th century lead at 5 Bq kg$^{-1}$ to 10 Bq kg$^{-1}$ $^{210}$Pb. Figure 5.14 shows the background spectra from a sample of de-ionised water in a 125 mL Azlon bottle to match the geometry of the NORM reference material that was counted for 250,000 seconds.
Figure 5.14- Background spectra of a sample of de-ionised water in a 125 mL Azlon bottle measured for 250,000 seconds on ‘Lancelot’.

There was no copper/cadmium liner as the sources assayed were typically of relatively low activity. ‘Lancelot’s’ carbon fibre layer window allows for the measurement of low energy $\gamma$ emissions such as $^{210}$Pb in the NORM samples. The detector has a relative efficiency of 65% at 1332 keV ($^{60}$Co) and resolution of 1.70 keV at 1332 keV ($^{60}$Co) (NPL internal Lancelot efficiency report). It incorporates a high-voltage power supply, preamplifier Canberra AFT research amplifier (6 $\mu$s shaping time), multi-channel analyser and uses the “PUR/DT” circuitry to correct for live time for pile-up and dead time. The collected spectra data were analysed using Canberra Genie (2000), while the peak areas were analysed using the Canberra Genie 2000 v2.1C software, with all peaks manually checked using the Interactive Peak Fitting application within this software. Dead time, pulse pile-up and background peak area corrections were all applied using the Canberra Genie 2000 v2.1C software.
5.7.1.1 Energy calibration

The detectors were initially calibrated for their full energy peak response using a $^{154}$Eu source with peak centroids set within 0.1 keV for $\gamma$ emissions with intensities in excess of 1%, using the evaluated energies from the Decay Data Evaluation Project.

Figure 5.15- Energy calibration spectra of ‘Lancelot’ performed using a $^{154}$Eu source (Reich, 2009).

5.7.1.2 Efficiency calibration

The absolute full-energy-peak efficiency of ‘Lancelot’ was derived based on measurements of an NPL mixed radionuclide solution (R08-03, June 2016: $^{241}$Am, $^{109}$Cd, $^{57}$Co, $^{139}$Ce, $^{51}$Cr, $^{113}$Sn, $^{85}$Sr, $^{137}$Cs, $^{54}$Mn, $^{65}$Zn, $^{60}$Co and $^{88}$Y) in the same geometry as the reference material samples (certificates in Appendix F). The sample format used was the 10 mL NPL mix ampoule was topped up to ~100 grams with 4 M HCl contained in a 125 mL Azlon bottle measured at a distance of 10 cm from the detector window, with a counting time of 50,000 seconds, to reflect
the geometry that the reference materials were measured in. The 10 cm distance used for the measurements allowed for the assumption that the effect of cascade summing to be negligible for the detector. Each sample was assayed twice, before and after the reference material sample measurements to take account of any detector drift. Looking at the detector response at lower energies from Figure 5.16 and 5.17 it is clear there is an advantage in using ‘Lancelot’ for the measurement of low energy γ-ray emissions such as $^{210}$Pb in the NORM samples.

![Figure 5.16- Efficiency response of ‘Lancelot’ shown on linear scale at different gamma-ray energies using the NPL standard mix source R08-03, $^{232}$Th, $^{226}$Ra, natU and $^{210}$Pb.](image)

161
Figure 5.17- Efficiency response of ‘Lancelot’ shown on logarithmic scale at different gamma-ray energies using the NPL standard mix source R08-03, $^{232}$Th, $^{226}$Ra, natU and $^{210}$Pb.

5.7.1.3 Detection limits for $\gamma$-ray spectrometry counting system

Table 5.8 shows, the lowest and highest values for the LLD are 90 to 380 counts from $^{208}$Tl (2614 keV) and $^{226}$Ra (186 keV), respectively. The MDA essentially converts peak counts at energy of interest at given efficiency into activity (Becquerel). From the table, MDAs for ‘Lancelot’ ranges from $0.4 \pm 0.1$ Bq for $^{137}$Cs to a maximum value of $3.5 \pm 1.5$ Bq for $^{226}$Ra and $^{40}$K. These values show the smallest amount of radioactivity that can be detected and distinguished from the blank at the respective energies.
<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>$\gamma$-ray energy (keV)</th>
<th>LLD (total counts)</th>
<th>MDA (Bq/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{226}$Ra</td>
<td>186.2</td>
<td>380 ± 160</td>
<td>3.5 ± 1.5</td>
</tr>
<tr>
<td>$^{214}$Pb</td>
<td>351.9</td>
<td>230 ± 100</td>
<td>0.4 ± 0.2</td>
</tr>
<tr>
<td>$^{208}$Tl</td>
<td>583.2</td>
<td>170 ± 70</td>
<td>0.5 ± 0.2</td>
</tr>
<tr>
<td>$^{214}$Bi</td>
<td>609.3</td>
<td>180 ± 80</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>$^{228}$Ac</td>
<td>911.2</td>
<td>180 ± 80</td>
<td>1.0 ± 0.4</td>
</tr>
<tr>
<td>$^{228}$Ac</td>
<td>968.9</td>
<td>140 ± 60</td>
<td>1.4 ± 0.5</td>
</tr>
<tr>
<td>$^{214}$Bi</td>
<td>1120.3</td>
<td>250 ± 110</td>
<td>3.2 ± 1.4</td>
</tr>
<tr>
<td>$^{40}$K</td>
<td>1460.8</td>
<td>150 ± 60</td>
<td>3.5 ± 1.5</td>
</tr>
<tr>
<td>$^{214}$Bi</td>
<td>1764.5</td>
<td>100 ± 40</td>
<td>1.8 ± 0.7</td>
</tr>
<tr>
<td>$^{208}$Tl</td>
<td>2614.5</td>
<td>90 ± 40</td>
<td>1.0 ± 0.4</td>
</tr>
</tbody>
</table>

Table 5.8- Detection limit for $\gamma$-spectrometry (‘Lancelot’) counting system used in the work for a counting time of 50,000 with a sample of deionised water.

5.7.2 Alpha spectrometry

The electroplated sources were counted by $\alpha$-spectrometry in an ORTEC Octete Plus $\alpha$-particle spectrometer with Passivated Implanted Planar Silicon (PIPS) detectors and Ortec Maestro, Multichannel Analyser (MCA) application software.

PIPS detectors are essentially 100% efficient if an $\alpha$-particle interacts with the detector surface, thus it was assumed that the detector records an event every time an $\alpha$-particle strikes its surface. However as alpha particles travel in random directions (isotropically) away from the source, not all particles will strike the detector surface. Thus, the counting efficiency is the fraction of total alpha radiation emitted by the source that is recorded by the detector. Although in this work a radioactive tracer is used, to trace the efficiency of the analysis, throughout the procedure used, it is useful to understand the efficiency of the detector from various detector distances, to know where to measure the source to obtain the best possible energy resolution and counting statistics for each measurement. This is of significance in low level NORM measurements, where due to low counting statistics, high measurement uncertainties, can produce unsuitable results.
Counting efficiency can be described as the fraction of the total alpha radiation emitted by the source that is recorded by the detector and is thus a function of size of the active area of source, distance between source and detector and radiation-sensitive area of detector (Krane, 1998). As the absolute counting efficiency is inversely proportional to the square of the distance between the source and the active area of the detector, there are substantial losses in efficiency for increasing detector-source distance. According to Canberra, (Canberra) a 450 mm² PIPS detector located 1 cm from the source has a theoretical efficiency of 36%, and it is expected that sources that are evenly distributed over the surface of a disc the same size as the detector will count at an efficiency of approximately 21%. In order to determine accurate efficiencies and to validate the detectors before carrying out measurements, a standard Eckert and Ziegler calibration source of known activity (total activity 600 Bq) mixed $^{241}$Am (200 Bq), $^{237}$NP (200 Bq) and $^{244}$Cm (200 Bq) source was used. From measuring the source at 1 cm, 5 cm and 10 cm, the following efficiencies were calculated 21.0 ± 1.2%, 5.2 ± 0.5% and 2 ± 0.5 %. The NORM sources were all counted 1 cm away from the detector.

5.7.2.1 Energy calibration

Prior to any $\alpha$-particle spectrometry measurements being carried out, all the detectors used were calibrated using the alpha emitting mix check source (Figure 5.18), in order to confirm a precise energy calibration. Using the check source utilizing energies of 4.78 MeV, 5.48 MeV and 5.80 MeV for $^{237}$Np, $^{241}$Am and $^{244}$Cm respectively, it was ensured that energies spanning a full range of interest were measured and peaks selected for calibration were well-defined singlet peaks, once the source was measured, the energy calibration was performed by plotting the centroid of the peaks against the known energies.
5.7.2.2 Alpha spectrometry peak fitting

In α-spectrometry the peaks should be near Gaussian shape (Krane, 2010) with a tail and typically backgrounds should be low. Using Maestro software to interpret the spectra, a region of interest was selected. The region of interest was selected for each peak where it was generally considered to start at the first positive change in slope and end in the second position change in the slope. Although it is possible to carry out this process using the software’s automated setting, it is best practice to carry out a visual inspection and carry out the process manually. Once the region of interest was selected, a simple integration, carried out using the analysis software was sufficient to describe the counts collected for each identified nuclide.

![Energy calibration spectrum for the α calibration source.](image)

Figure 5.18- Energy calibration spectrum for the α calibration source.
5.7.2.3 Background correction

In α-particle spectrometry measurements of low level environment samples, such as the NORM samples measured in this work, background contamination is critical and should be considered in order to establish results with an acceptable levels of uncertainty. Background measurements were carried out by placing a clean disc in the detector and measuring with a source and accumulating gross counts in the 3 MeV to 7 MeV region for 200,000 seconds with the clear discs counted in sample designated holders for each detector. Background measurements were taken before each measurement carried in this EngD thesis. At NPL detectors 17 to 24 are used for research work (for validation see Appendix A), with this in mind initial backgrounds were taken to choose what detectors to use for environmental level measurements. The data shown in Figure 5.19, shows high background levels in detector 17 (not suitable for low level environmental measurements), thus for the NORM work it was decided that detectors 18 and 19 would be used to measure the Uranium series, with 20 and 21 being used to measure the Thorium series and 23 being used for the assay of polonium. This system was used to make sure that background contamination did not interfere with any of regions of interest for the selected radionuclides measured in this work.
Figure 5.19- Bar chart of detector number versus background counts per second for $^{238}\text{U}$, $^{232}\text{Th}$ and $^{236}\text{Pu}$ between 3 to 7 MeV for a counting time of 200,000 seconds.

5.7.2.4 Alpha Spectrometry nuclide quantification

In $\alpha$-particle spectrometry it is possible to identify nuclides quantitatively by a number of methods using efficiencies (as discussed previously) with a calibrated standard, where the requirement would be for the geometry of the source to be kept constant. In this thesis for both the NORM measurements and Np work, the quantification was carried out using a yield tracer. In analytical chemistry, as discussed in Chapter 3, the most common method to determine the yield of a source is to add a known amount of yield tracer to the sample early in the procedure in order to trace recovery and thus acting as a test of the efficiency of the process. In practice, it is not the activity of the source that is of interest in this work, it is the activity of the original
sample that has been subjected to a series of chemical processing steps before preparation of the source. If it is assumed that there is complete equilibrium between sample and tracer isotopes, the technique of isotope dilution using a yield tracer can be used to identify the ratio of the unknown nuclide in the sample to that of the tracer isotope. Thus, leading to a very precise measurement, which is independent from detector efficiency or instrumentational drift.

Using Equation 5.1, the specific activity of the sample can be calculated using the known added yield tracer value, by determination of the net count rates under both the tracer peak and unknown activity of isotope X:

\[ A_x = A_0 \times \left[ \frac{(net\ cpm)_x}{(net\ cpm)_o} \right] \times \frac{1}{wt(vol)} \]  

(Equation 5.1)

where:

- \( A_x \) = specific activity of the nuclide
- \( A_0 \) = activity of the tracer added
- Subscripts \( x \) and \( o \) refer to the unknown and tracer respectively.

5.7.2.5 Source Preparation of alpha spectrometry sources

In order for the samples to be counted by \( \alpha \)-particle spectrometry they must be deposited onto a metallic substrate (i.e. the cathode of the electrolytic cell) commonly a stainless steel disc to make sure that the radioactive specimen is in an immobilised state, (Hansen, 1959). This is vital in making sure contamination does not occur in the counter chamber under vacuum conditions or on the individual. Electrodeposition is the most common technique of source preparation for routine measurements (Garcia-Torano, 2006). The source must be as uniform and thin as possible in order to obtain high energy resolution spectra and to produce
accurate measurements (Crespo, et al, 2003). Once samples are spiked with a chemical yield tracer and are chemically separated using appropriate radiochemical separation techniques such as extraction chromatography as described in section 5.6.2, the sample is then evaporated to dryness on a hot plate at 180 °C. Once evaporated to incipient dryness, the sample is then dissolved in 2 mL of 15.8 M concentrated HNO₃, and then the sample is once again evaporated to incipient dryness and two drops of H₂O₂ (Hydrogen Peroxide) are added to destroy any remaining organics and iodide bonds within the sample, this step is repeated at least twice before the electrodeposition process takes place.

According to Hansen (1959), the electrodeposition from aqueous media of uranium and other actinides occurs by a precipitation reaction within a hydroxyl ions layer formed at the cathode surface. Using the Hallstadius method (1984), the stainless-steel disc which is 2.5 cm in diameter and 1 mm thick is used as the cathode of the electrolysis cell while the electrolytes used are Sulphuric acid (H₂SO₄), along with Na₂SO₄ while the pH is set to ~2.3. The electrolytes used are in order to prevent the adsorption of the low mass concentration of most actinides onto the wall of the electrodeposition cell (Crespo, et al, 2009). Platinum wire is used as the anode (Ferrero Calabuig, et al, 1998b). The wire was 1 mm diameter wire folded in the base into spiral shape. Only the lower part of the straight wire and the spiral were submersed in the electrolyte. The process utilised a current density of 0.52 A. cm⁻² and voltage of 10 V, with the process running for two hours. Once the electroplating process is completed, a minute before the cells are switched off 1 mL of 4 M NaOH (Sodium Hydroxide) is added to each cell to make certain that the plating is immobilised on the disc. Once the power pack is switched off, the solution used for electrodeposition is transferred into a bottle labelled with its sample number and radionuclide source and is either taken for disposal or reused if the plating has not worked to a desired effect. With the plated disc removed from the lid and then once again
cleaned with a few drops of acetone, it is placed on a hot plate to dry and into a labelled petri dish.

Unlike actinides such as uranium, thorium and plutonium which require electrodeposition, other elements can undergo internal electrolysis (spontaneous deposition). In the measurements taken for the analysis of the NORM reference materials, Po will be analysed by α-spectrometry. One of the characteristics of Po is its ease of deposition, although spontaneous deposition is simpler than electrodeposition, spontaneous deposition has the disadvantage that the electrode potential is fixed by the selection of the metal. Since the deposition potential for Bi is close to that of Po, in many cases Bi(RaE) is also deposited. Marckwald (1905) found that Po deposited spontaneously on a Silver substrate from HCl solution yield 90% recoveries typically, samples were often treated with reducing agents such as ascorbic acid and hydroxylamine hydrochloride are added to prevent interference with Fe. The pH is adjusted to two with ammonia solution, the silver coated disc is then inserted into the solution and the Po self-plates for a two-hour period at the same current and voltage settings as the actinide deposition outlined above (Vajda, et al, 1997; Vreček, et al, 2004; Miura, et al, 2000).

5.7.2.6 Detection limits α-spectrometry

<table>
<thead>
<tr>
<th>Detector</th>
<th>Limit of detection (Bq kg(^{-1})) at 95% confidence over 50,000 counts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(^{238})U</td>
</tr>
<tr>
<td>18</td>
<td>0.34</td>
</tr>
<tr>
<td>19</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Table 5.9 Limit of detection for U, Th and Po isotopes in detectors 18 and 19 for a count time of 100,000 seconds using a \(^{236}\)U, \(^{229}\)Th and \(^{209}\)Po tracer added to 1 gram of blank sand material.
5.7.3 Inductively Coupled Plasma Mass Spectrometry

5.7.3.1 Source preparation for ICP-QQQ-MS measurements

The 1 mL aliquot was diluted up to a total volume of 10 mL with 2% (v/v) HNO₃ prior to measurement by ICP-QQQ-MS. The Agilent 8800 ICP-QQQ-MS was fitted with a quartz double-pass spray chamber and a MicroMist nebuliser (Glass Expansion, Melbourne, Australia) and nickel sample and skimmer cones (Crawford Scientific, South Lanarkshire, UK). The instrument was operated in single quadrupole mode throughout, and tuned daily using a mixed 1 μg/g standard solution of Li, Mg, Ce, Co, Y and Tl and a performance report produced to give an early indication of instrument sensitivity. No additional thorium and uranium-specific tuning was carried out.

5.8 Experimental Results and Discussion

5.8.1 Gamma-ray analysis and nuclide identification

All of the reference material samples were measured, instead of measuring a randomly selected subset of samples. The between sample variance was determined by measuring all of the samples of each reference material once by high-resolution γ-ray spectrometry where comparison of the net peak areas of the main energy γ lines for the three selected reference materials was taken. This was carried out to ensure no hot spots were present, and that the samples were homogenous and were a true representation of each material.

The coefficient of variation was determined by dividing the standard deviation of the number of counts for a specific energy divided by the average number of counts and then multiplied by 100 to derive the coefficient of variation in %.
5.8.1.1 Sample homogeneity

Tuff

Once processed the same amount of Tuff was filled in six identical containers. Each of these containers was measured at 84,400 seconds. Then the spectra were analysed and net peak counts of the most intense peaks were compared. The coefficient of variation for each nuclide is up to 1.04 % for $^{40}$K.

Figure 5.20- Tuff samples in identical containers measured for hot spots by $\gamma$-ray spectrometry.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>$^{208}$Tl</th>
<th>$^{214}$Pb</th>
<th>$^{214}$Bi</th>
<th>$^{228}$Ac</th>
<th>$^{40}$K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy [keV]</td>
<td>583.2</td>
<td>351.9</td>
<td>609.3</td>
<td>911.2</td>
<td>1460.8</td>
</tr>
<tr>
<td>Sample # of counts</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>16751 ± 129</td>
<td>25074 ± 158</td>
<td>18135 ± 134</td>
<td>11241 ± 106</td>
<td>17093 ± 130</td>
</tr>
<tr>
<td>2</td>
<td>16804 ± 130</td>
<td>24937 ± 158</td>
<td>18132 ± 135</td>
<td>11362 ± 107</td>
<td>16578 ± 129</td>
</tr>
<tr>
<td>3</td>
<td>16776 ± 130</td>
<td>25439 ± 160</td>
<td>18252 ± 135</td>
<td>11371 ± 107</td>
<td>16996 ± 130</td>
</tr>
<tr>
<td>4</td>
<td>16685 ± 129</td>
<td>24965 ± 158</td>
<td>18080 ± 134</td>
<td>11153 ± 106</td>
<td>16944 ± 130</td>
</tr>
<tr>
<td>5</td>
<td>16750 ± 129</td>
<td>24801 ± 157</td>
<td>18248 ± 134</td>
<td>11345 ± 106</td>
<td>16876 ± 130</td>
</tr>
<tr>
<td>6</td>
<td>16800 ± 130</td>
<td>24803 ± 157</td>
<td>18134 ± 135</td>
<td>11234 ± 107</td>
<td>16850 ± 130</td>
</tr>
<tr>
<td>Average</td>
<td>16761 ± 130</td>
<td>25003 ± 158</td>
<td>18164 ± 135</td>
<td>11284 ± 107</td>
<td>16890 ± 130</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>44</td>
<td>237</td>
<td>70</td>
<td>88</td>
<td>176</td>
</tr>
<tr>
<td>Coefficient of Variation</td>
<td>0.26</td>
<td>0.95</td>
<td>0.39</td>
<td>0.78</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Table 5.10- Coefficient of variation for Tuff samples.
TiO$_2$

The same amount of TiO$_2$ was filled in six identical containers. Each of these containers were measured for 30,000 seconds. Then the spectra were analysed and net peak counts of the most intense peaks were compared. The coefficient of variation for each nuclide is up to 1%.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>$^{208}$Tl</th>
<th>$^{214}$Pb</th>
<th>$^{214}$Bi</th>
<th>$^{228}$Ac</th>
<th>$^{40}$K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy [keV]</td>
<td>583.2</td>
<td>351.9</td>
<td>609.3</td>
<td>911.2</td>
<td>1460.8</td>
</tr>
<tr>
<td>Sample # of counts</td>
<td>1</td>
<td>7682 ± 88</td>
<td>9173 ± 96</td>
<td>6775 ± 82</td>
<td>5524 ± 74</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>7689 ± 88</td>
<td>9230 ± 96</td>
<td>6801 ± 82</td>
<td>5495 ± 74</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>7701 ± 88</td>
<td>9306 ± 96</td>
<td>6828 ± 83</td>
<td>5600 ± 75</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>7790 ± 88</td>
<td>9219 ± 96</td>
<td>6789 ± 82</td>
<td>5489 ± 74</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>7648 ± 87</td>
<td>9389 ± 97</td>
<td>6801 ± 82</td>
<td>5510 ± 74</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>7592 ± 87</td>
<td>9210 ± 96</td>
<td>6793 ± 82</td>
<td>5442 ± 74</td>
</tr>
<tr>
<td>Average</td>
<td>7684 ± 88</td>
<td>9255 ± 96</td>
<td>6798 ± 82</td>
<td>5510 ± 74</td>
<td>9761 ± 99</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>65</td>
<td>79</td>
<td>18</td>
<td>52</td>
<td>57</td>
</tr>
<tr>
<td>Coefficient of Variation $%$</td>
<td>0.85</td>
<td>0.85</td>
<td>0.26</td>
<td>0.95</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Table 5.11- Coefficient of variation for TiO$_2$ samples.

Sand

The same amount of Sand was filled in six identical containers. Each of these containers was measured for 30,000 seconds. Then the spectra were analysed and net peak counts of the most intense peaks were compared. The coefficient of variation for each nuclide is up to 1% (for $^{40}$K).

Once homogeneity measurements were conducted and the results were analysed the coefficient variations of the three samples were all deemed to be within the limits, the samples were bottled up and were deemed a true representation of the starting bulk material.
<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>$^{208}$Tl</th>
<th>$^{214}$Pb</th>
<th>$^{214}$Bi</th>
<th>$^{228}$Ac</th>
<th>$^{40}$K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy [keV]</td>
<td>583.18</td>
<td>351.93</td>
<td>609.3</td>
<td>911.196</td>
<td>1460.8</td>
</tr>
<tr>
<td>Sample # of counts</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2923 ± 54</td>
<td>4329 ± 66</td>
<td>1929 ± 44</td>
<td>1827 ± 43</td>
<td>16129 ± 127</td>
</tr>
<tr>
<td>2</td>
<td>2910 ± 54</td>
<td>4423 ± 67</td>
<td>1901 ± 44</td>
<td>1862 ± 43</td>
<td>16089 ± 127</td>
</tr>
<tr>
<td>3</td>
<td>2896 ± 54</td>
<td>4410 ± 66</td>
<td>1908 ± 44</td>
<td>1802 ± 43</td>
<td>16101 ± 127</td>
</tr>
<tr>
<td>4</td>
<td>2859 ± 53</td>
<td>4391 ± 66</td>
<td>1911 ± 44</td>
<td>1809 ± 43</td>
<td>16108 ± 127</td>
</tr>
<tr>
<td>5</td>
<td>2910 ± 54</td>
<td>4408 ± 66</td>
<td>1923 ± 44</td>
<td>1820 ± 43</td>
<td>16201 ± 127</td>
</tr>
<tr>
<td>6</td>
<td>2929 ± 54</td>
<td>4421 ± 66</td>
<td>1907 ± 44</td>
<td>1811 ± 43</td>
<td>16198 ± 127</td>
</tr>
<tr>
<td>Average</td>
<td>2905 ± 54</td>
<td>4397 ± 66</td>
<td>1913 ± 44</td>
<td>1821 ± 43</td>
<td>16138 ± 127</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>25</td>
<td>35</td>
<td>11</td>
<td>23</td>
<td>50</td>
</tr>
<tr>
<td>Coefficient of Variation %</td>
<td>0.86</td>
<td>0.80</td>
<td>0.56</td>
<td>1.01</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Table 5.12- Coefficient of variation for Sand samples.
Figure 5.21- Example of the $\gamma$-ray spectra of four Sand samples taken on ‘Lancelot’ for 30,000 seconds to determine the coefficient of variation between the material.
5.8.1.2 Sample gamma-ray spectra activity determination

Each sample was assayed twice using the semi-planar germanium γ-ray spectrometer ‘Lancelot’ for measurement of specific activity concentration. Counting times for each sample was for 50,000 seconds, the measurements were analysed looking at the peak centroid energy of interest from the $^{232}$Th and $^{238}$U decay chains, but also from $^{40}\text{K}$. Daughter radionuclides from the respective chains in each of the samples were identified by comparing their γ ray energies with known energies from published nuclear decay data. Only γ rays that were not subject to cascade summing were used to calculate activity values (Table 5.13 and 5.14).

<table>
<thead>
<tr>
<th>$^{238}\text{U}$ series Radionuclide</th>
<th>Energy (keV)</th>
<th>Emission probability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{226}\text{Ra}$</td>
<td>186.2 (13)</td>
<td>3.6 (6)</td>
</tr>
<tr>
<td>$^{214}\text{Pb}$</td>
<td>295.2 (2)</td>
<td>18.2 (2)</td>
</tr>
<tr>
<td></td>
<td>351.9 (2)</td>
<td>35.1 (4)</td>
</tr>
<tr>
<td>$^{214}\text{Bi}$</td>
<td>609.3 (7)</td>
<td>44.6 (5)</td>
</tr>
<tr>
<td></td>
<td>1120.3 (10)</td>
<td>14.7 (2)</td>
</tr>
<tr>
<td></td>
<td>1764.5 (14)</td>
<td>15.1 (2)</td>
</tr>
<tr>
<td>$^{238}\text{U}$ (via $^{234m}\text{Pa}$)</td>
<td>766.4 (2)</td>
<td>0.2 (12)</td>
</tr>
<tr>
<td></td>
<td>1001.0 (3)</td>
<td>0.8 (10)</td>
</tr>
<tr>
<td>$^{40}\text{K}$</td>
<td>1460.8 (6)</td>
<td>10.6 (18)</td>
</tr>
</tbody>
</table>

Table 5.13- γ-ray energies and emission probabilities of isotopes of interest in $^{238}\text{U}$ series and $^{40}\text{K}$ (data taken from DDEP).
<table>
<thead>
<tr>
<th>$^{232}$Th series Radionuclide</th>
<th>Energy (keV)</th>
<th>Emission probability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{228}$Ac</td>
<td>338.3 (3)</td>
<td>11.3 (12)</td>
</tr>
<tr>
<td></td>
<td>911.2 (4)</td>
<td>25.9 (4)</td>
</tr>
<tr>
<td></td>
<td>968.9 (17)</td>
<td>15.8 (3)</td>
</tr>
<tr>
<td>$^{212}$Pb</td>
<td>238.6 (2)</td>
<td>43.3 (3)</td>
</tr>
<tr>
<td></td>
<td>300.1 (10)</td>
<td>3.3 (4)</td>
</tr>
<tr>
<td>$^{212}$Bi</td>
<td>727.3 (9)</td>
<td>6.65 (4)</td>
</tr>
<tr>
<td></td>
<td>1 620.7 (10)</td>
<td>1.51 (3)</td>
</tr>
<tr>
<td>$^{208}$Tl</td>
<td>583.2 (2)</td>
<td>30.4 (2)</td>
</tr>
<tr>
<td></td>
<td>2614.5 (3)</td>
<td>99.8 (4)</td>
</tr>
</tbody>
</table>

Table 5.14- $\gamma$-ray energies and emission probabilities of isotopes of interest in $^{232}$Th series (data taken from DDEP).

Figure 5.22 shows the spectra taken from the measured samples, from the spectra the $\gamma$ ray transitions from the $^{232}$Th and $^{238}$U are depicted. Clear peaks that are visible in the spectra include $^{212}$Pb, $^{212}$Bi, $^{228}$Ac and $^{208}$Tl from the Thorium series and $^{226}$Ra, $^{214}$Pb, $^{214}$Bi from the Uranium series, as well as the 1461 keV line from $^{40}$K.
Figure 5.22- $\gamma$ ray spectra of the Sand, TiO$_2$ and Tuff materials using the ‘Lancelot’ HPGe spectrometer at NPL measured for 50,000 seconds.
5.8.1.3 Gamma-spectrometry nuclide identification

The γ-ray spectrometry results of the three matrices are displayed in Tables 5.15 and 5.16.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Technique</th>
<th>Sand (Bq/kg) (k=2)</th>
<th>TiO₂ (Bq/kg) (k=2)</th>
<th>Tuff (Bq/kg) (k=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>²³²⁶Th (via ²²⁸Ac)</td>
<td>γ-ray spectrometry</td>
<td>7.0 ± 1.0</td>
<td>21,200 ± 1,400</td>
<td>350 ± 10</td>
</tr>
<tr>
<td>²³²³Th (via ²¹²Pb)</td>
<td>γ-ray spectrometry</td>
<td>7.0 ± 0.7</td>
<td>19,600 ± 1,300</td>
<td>354 ± 24</td>
</tr>
<tr>
<td>²³²³Th (via ²¹²Bi)</td>
<td>γ-ray spectrometry</td>
<td>7.1 ± 1.0</td>
<td>19,200 ± 711</td>
<td>356 ± 11</td>
</tr>
<tr>
<td>²³²³Th (via ²⁰⁸Tl)</td>
<td>γ-ray spectrometry</td>
<td>7.0 ± 0.6</td>
<td>18,500 ± 214</td>
<td>351 ± 6</td>
</tr>
</tbody>
</table>

Table 5.15- Thorium (4n) series results.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Technique</th>
<th>Sand (Bq/kg) (k=2)</th>
<th>TiO₂ (Bq/kg) (k=2)</th>
<th>Tuff (Bq/kg) (k=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>²³⁵⁸U (via ²³⁴⁰Pa)</td>
<td>γ-ray spectrometry</td>
<td>&lt;34</td>
<td>&lt;21</td>
<td>426 ± 92</td>
</tr>
<tr>
<td>²³⁵U</td>
<td>γ-ray spectrometry</td>
<td>&lt;2</td>
<td>&lt;7</td>
<td>20 ± 3</td>
</tr>
<tr>
<td>²²⁶⁶Ra (direct)</td>
<td>γ-ray spectrometry</td>
<td>117 ± 23</td>
<td>28,200 ± 2,000</td>
<td>249 ± 30</td>
</tr>
<tr>
<td>²²⁶⁶Ra (via ²¹⁴Pb)</td>
<td>γ-ray spectrometry</td>
<td>85 ± 9</td>
<td>26,600 ± 620</td>
<td>213 ± 7</td>
</tr>
<tr>
<td>²²⁶⁶Ra (via ²¹⁴Bi)</td>
<td>γ-ray spectrometry</td>
<td>84 ± 3</td>
<td>29,000 ± 2,000</td>
<td>188 ± 6</td>
</tr>
</tbody>
</table>

Table 5.16- Uranium (4n+2) series results.

It must be noted that it is difficult to make accurate ²¹⁰Pb determinations based on direct γ-ray spectrometry of such samples and these results have not been included in this work. This is due to the correction factor for self-attenuation which results in the calibration factor varying by a
factor of 16 over the matrices considered (Landsberger and Millsap, 2014). In order to determine precise $^{210}\text{Pb}$ values further radiochemical techniques are recommended.

In the case of the Sand and Tuff material even though the bottles which contained the samples were sealed with PVC tape, based on the activity ratios of the decay products to the parent, the decay products of $^{226}\text{Ra}$, such as $^{222}\text{Rn}$ (which has a 3.8-day half-life should take approximately 27 days to reach equilibrium with its parent ($^{226}\text{Ra}$) in the uranium chain) are not contained by the matrix and only the 186.2 keV line can reliably be used for assay. Any loss in Rn would underestimate the amount of $^{226}\text{Ra}$ present.

**5.8.1.4 $^{235}\text{U}$ (185.72 keV) and $^{226}\text{Ra}$ (186.21) peak correction**

The contribution of counts in the 186 keV peak can be determined by using the expected, natural $^{235}\text{U}/^{238}\text{U}$ isotopic ratio when the $^{226}\text{Ra}$ is in radioactive equilibrium with its parent $^{238}\text{U}$ (Gilmore, 2008). The half-lives, isotopic abundance and $\gamma$-emission probability for $^{238}\text{U}/^{235}\text{U}$ and $^{226}\text{Ra}$ are given in Table 5.17 (Oliver, et al, 2007);

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Abundance (%)</th>
<th>$T_{1/2}$ (yr)</th>
<th>$\gamma$-ray energy (keV)</th>
<th>$\gamma$-ray emission probability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{235}\text{U}$</td>
<td>0.720%</td>
<td>$7.0 \times 10^8$ y</td>
<td>185.7 (5) 143.8 (2) 163.4 (2) 205.3 (2)</td>
<td>57.2 (5) 10.9 (8) 5.0 (4) 5.0 (5)</td>
</tr>
<tr>
<td>$^{226}\text{Ra}$</td>
<td>daughter</td>
<td>1600 (7) y</td>
<td>186.2 (13)</td>
<td>3.6 (6)</td>
</tr>
</tbody>
</table>

Table 5.17- Table showing uranium isotopes abundance, half-life and $\gamma$-ray emission probability of the Peak 186 keV discrete transition of the decay of $^{235}\text{U}$ and $^{226}\text{Ra}$.
If radioactive equilibrium is achieved, then the activities of the $^{238}$U and its decay chain daughter $^{226}$Ra are equal.

Therefore, at equilibrium:

$$A_{U^{238}} = \lambda_{U^{238}}N_{U^{238}} = \frac{\ln 2}{4.4683 \times 10^9 \times 365 \times 24 \times 60 \times 60} \cdot 99.3 \ (Equation \ 5.2)$$

$$A_{U^{235}} = \lambda_{U^{235}}N_{U^{235}} = \frac{\ln 2}{0.7038 \times 10^9 \times 365 \times 24 \times 60 \times 60} \cdot 0.7 \ (Equation \ 5.3)$$

These values can be used to calculate $\gamma$ ray production rates from $^{235}$U and $^{226}$Ra in the samples assuming 100 atoms of natural uranium:

$$\gamma_{Ra^{226}} = (4.88 \times 10^{-16} \ dis./s) \cdot (0.063 \ \gamma/\dis) = 1.60 \times 10^{-17} \gamma/s \ (Equation \ 5.4)$$

$$\gamma_{U^{235}} = (2.248 \times 10^{-17} \ dis./s) \cdot (0.53 \ \gamma/\dis) = 1.19 \times 10^{-17} \gamma/s \ (Equation \ 5.5)$$

The individual contributions from the $^{235}$U and $^{226}$Ra to the $\gamma$ ray energy can be quantified, the ratio can be expressed as follows:

$$\frac{\gamma_{Ra^{226}}}{\gamma_{U^{235}}} = \frac{1.60 \times 10^{-17} \gamma/s}{1.19 \times 10^{-17} \gamma/s} = 1.34 \ (Equation \ 5.6)$$

∴ it can be expressed as:

$$\frac{\gamma_{Ra^{226}}}{\gamma_{(Ra^{226} + U^{235})}} = \frac{1.60 \times 10^{-17} \gamma/s}{(1.60 + 1.19) \times 10^{-17} \gamma/s} = 0.573 \ (Equation \ 5.7)$$
\[
\frac{Y_{U^{235}}}{Y_{(Ra^{226} + U^{235})}} = \frac{1.60 \times 10^{-17} \, y/s}{(1.60 + 1.19) \times 10^{-17} \, y/s} = 0.427 \quad (Equation \ 5.8)
\]

Therefore, the total contributions to the count rate at γ-ray energy of 186 keV from \(^{226}\)Ra and \(^{235}\)U is 57.3% and 42.7% respectively under secular equilibrium conditions. Multiplying the reported \(^{226}\)Ra concentration by 0.573 should therefore yield the correct \(^{226}\)Ra concentration via the 186 keV γ-ray intensity.

5.8.1.5 \(^{228}\)Ac (1459.2 keV) and \(^{40}\)K (1460.8 keV)

In addition to the peak interferences with \(^{226}\)Ra and \(^{235}\)U, there is a peak interference with the 4n Thorium series decay product \(^{228}\)Ac and \(^{40}\)K, leading to an overestimation in the activity of \(^{40}\)K. As shown in Table 5.15 \(^{228}\)Ac has several other discrete peak energies, thus using the \(^{232}\)Th standard used for the detector efficiency work, the ratio between the respective peaks can be determined. The corresponding peak energy of \(^{228}\)Ac at 911 keV is 27.7% and can be compared with the \(^{40}\)K 1459 keV obtain this ratio.

Using the following:

\[
\left[ \frac{Counts_{1459 \, keV}}{Counts_{911 \, keV}} \right]^{Th}_{\text{Sample}} = \left[ \frac{Counts_{1459 \, keV}}{Counts_{911 \, keV}} \right]^{Th}_{\text{Sample}} \quad (Equation \ 5.9)
\]

∴ it can be expressed as:

\[
Counts_{1459 \, keV} = \left[ \frac{Counts_{1459 \, keV}}{Counts_{911 \, keV}} \right]^{Th}_{\text{Sample}} \times Counts_{911 \, keV} = x \quad (Equation \ 5.10)
\]
Thus by subtracting the counts \( x \) at 1459.2 keV from the \(^{40}\text{K} 1460.2 \text{ keV}, \) the true counts for \(^{40}\text{K} \) can be derived.

The corrected \(^{40}\text{K} \) values for each of the reference materials is as follows:

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Technique</th>
<th>Sand (Bq/kg) ((k=2))</th>
<th>TiO(_2) (Bq/kg) ((k=2))</th>
<th>Tuff (Bq/kg) ((k=2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{40}\text{K} )</td>
<td>(\gamma)-ray spectrometry</td>
<td>190 ± 10</td>
<td>2.00 ± 0.03</td>
<td>2160 ± 380</td>
</tr>
</tbody>
</table>

Table 5.18. \(^{40}\text{K} \) activity concentration of each reference material.

5.8.1.6 Specific activity concentration based on \(\gamma\)-ray spectrometry

The specific activity concentration was calculated using like-for-like calibration factors for \(^{226}\text{Ra},^{235}\text{U}\) and \(^{210}\text{Pb} \). In the case of the decay progeny of \(^{226}\text{Ra} \), measurement of the

\[ ^{222}\text{Rn} \rightarrow ^{218}\text{Po} \rightarrow ^{214}\text{Pb} \rightarrow ^{214}\text{Bi} \rightarrow ^{214}\text{Po} \rightarrow ^{210}\text{Pb} \]

sub-series may be compromised potentially by losses of \(^{222}\text{Rn} \) (as might be expected from outgassing) and therefore calibration factors were derived based on the mixed radionuclide standard via a measured calibration curve (Figure 5.23).
Figure 5.23 - NPL mix, $^{210}$Pb, $^{226}$Ra, $^{232}$Th and $^{nat}$U showing peak centroid positions in channel numbers corresponding to absolute $\gamma$-ray energies, only $\gamma$ rays that were not subject to cascade summing were used to calculate activity values, see Tables 5.13 and 5.14.
In order to transform the efficiency derived using aqueous standards to that of the sample (Tuff, TiO\textsubscript{2} or sand), a GEANT 4 model (Figure 5.24) was developed using SWORD v5.0, (which is discussed further in Appendix E) (Gwon, 2007). The elemental compositions used as input to the model were based on the results of the Scanned Electron Microscope analysis (Figure 5.26 to 5.28), with the detector components being outlined in Table 5.19 based largely on manufacturer provided detector dimensions supplemented by previous experience in modelling the same detector. The model was unchanged between runs other than the composition of the source and was validated by comparison with the measured calibration curve and agreement achieved to $\pm 2\%$ ($k=2$) or better above 100 keV. Below 100 keV there is an agreement of $\pm 5\%$ ($k=2$), thus increasing the uncertainty on the measurement for $^{210}\text{Pb}$ (Figure 5.25).
Figure 5.25- Modelled calibration curve derived using SWORD v5, where the X-axis is shown on log scale. Across the range the modelled efficiency is within 5 % of the measured efficiency, and only deviates significantly at lower energies. Labelled points indicate the measured calibration curve using the NPL Mix Standard.

<table>
<thead>
<tr>
<th>Element</th>
<th>% (k=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>44.1 ± 0.9</td>
</tr>
<tr>
<td>Ti</td>
<td>41.7 ± 0.9</td>
</tr>
<tr>
<td>S</td>
<td>9.2 ± 0.4</td>
</tr>
<tr>
<td>Fe</td>
<td>2.8 ± 0.2</td>
</tr>
<tr>
<td>H</td>
<td>2.2 ± 0.1</td>
</tr>
</tbody>
</table>

Figure 5.26- Back-scattered electron image of TiO$_2$ and its detected elemental composition.
Figure 5.27- Back-scattered electron image of Tuff and its detected elemental composition.

<table>
<thead>
<tr>
<th>Element</th>
<th>% (k=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>34.4 ± 0.9</td>
</tr>
<tr>
<td>K</td>
<td>19.6 ± 0.8</td>
</tr>
<tr>
<td>Ca</td>
<td>17.6 ± 0.8</td>
</tr>
<tr>
<td>Al</td>
<td>12.3 ± 0.7</td>
</tr>
<tr>
<td>Fe</td>
<td>10.7 ± 0.6</td>
</tr>
<tr>
<td>Ti</td>
<td>1.4 ± 0.2</td>
</tr>
</tbody>
</table>

Figure 5.28- Back-scattered electron image of Sand and its detected elemental composition.

<table>
<thead>
<tr>
<th>Element</th>
<th>% (k=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>60.2 ± 1.0</td>
</tr>
<tr>
<td>O</td>
<td>21.1 ± 0.7</td>
</tr>
<tr>
<td>Ca</td>
<td>12.1 ± 0.6</td>
</tr>
<tr>
<td>Mg</td>
<td>4.3 ± 0.3</td>
</tr>
<tr>
<td>Al</td>
<td>1.1 ± 0.2</td>
</tr>
<tr>
<td>Fe</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>Item</td>
<td>Material</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>Detector front window</td>
<td>Carbon fibre</td>
</tr>
<tr>
<td>Detector outer case</td>
<td>Carbon fibre</td>
</tr>
<tr>
<td>Detector</td>
<td>Germanium</td>
</tr>
<tr>
<td>Detector bulletisation</td>
<td>Germanium</td>
</tr>
<tr>
<td>Detector dead layer</td>
<td>Germanium</td>
</tr>
<tr>
<td>Coaxial well</td>
<td>Vacuum</td>
</tr>
<tr>
<td>Coaxial well end</td>
<td>Vacuum</td>
</tr>
<tr>
<td>Copper liner</td>
<td>Copper</td>
</tr>
<tr>
<td>Source mount holder</td>
<td>Polymethyl methacrylate</td>
</tr>
</tbody>
</table>

Table 5.19- Description of detector components for ‘Lancelot’ that make up the SWORD model.

To further reduce the measurement uncertainty of the samples a weighted mean analysis is carried out to determine the activity of the independent discrete γ lines from each decay chain.

Figures 5.29 to 5.34 show the activity values observed, with the horizontal dotted lines displaying the weighed mean of the individual data points. The weighed means of the $^{232}$Th ($^{228}$Ac, $^{212}$Pb and $^{208}$Tl) and $^{238}$U ($^{226}$Ra, $^{214}$Pb and $^{214}$Bi) (excluding $^{210}$Pb) were calculated using the following equation:

$$M_w = \frac{\sum_i w_i M_i}{\sum_i w_i} \quad (Equation \, 5.11)$$

With the standard error being derived by (further details in Appendix D):
\[ \sigma_{M_w} = \sqrt{\frac{1}{w_1 + w_2 + \cdots + w_n}} \] (Equation 5.12)

Figure 5.29- Weighted mean plot for thorium from Sand reference material, the horizontal bar lines represent the weighted mean value of 7.1 ± 0.3 Bq/kg.
Figure 5.30- Weighted mean plot for uranium from Sand reference material, using the corrected $^{226}\text{Ra}$ data point which is still above the weighted mean line after removing the $^{235}\text{U}$ contribution, indicating slight enrichment, the horizontal bar lines represent the weighted mean value of $80.5 \pm 0.6 \text{ Bq/kg}$.
Figure 5.31- Weighted mean plot for thorium from TiO$_2$ reference material, the horizontal bar lines represent the weighted mean value of $19.1 \pm 0.3$ kBq/kg. This plot shows possible fractionation of $^{228}$Ra, due to a higher activity of $^{228}$Ac than $^{212}$Bi and $^{208}$Tl, as they have not had enough time to get into secular equilibrium with $^{228}$Ra $\rightarrow$ $^{228}$Ac since separation.
Figure 5.32- Weighted mean plot for uranium from TiO$_2$ reference material, the horizontal bar lines represent the weighted mean value of 28.0 ± 0.6 kBq/kg. Note no correction required for $^{226}$Ra.
Figure 5.33- Weighted mean plot for thorium from Tuff reference material indicating secular equilibrium, the horizontal bar lines represent the weighted mean value of $350.4 \pm 0.9$ Bq/kg.
Figure 5.34- Weighted mean plot for uranium from Tuff reference material indicating secular equilibrium, the horizontal bar lines represent the weighted mean value of $203.8 \pm 0.9$ Bq/kg.

### 5.8.2 Alpha Spectrometry and ICP-MS analysis and nuclide identification

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Technique</th>
<th>Sand (Bq/kg) ($k=2$)</th>
<th>TiO$_2$ (Bq/kg) ($k=2$)</th>
<th>Tuff (Bq/kg) ($k=2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{232}$Th</td>
<td>ICP-MS*</td>
<td>7.2</td>
<td>15.6</td>
<td>484</td>
</tr>
<tr>
<td>$^{232}$Th</td>
<td>$\alpha$-spectrum</td>
<td>3.1 ± 0.1</td>
<td>9.0 ± 0.4</td>
<td>326 ± 18</td>
</tr>
<tr>
<td>$^{228}$Th</td>
<td>$\alpha$-spectrum</td>
<td>5.0 ± 0.2</td>
<td>3430 ± 110</td>
<td>321 ± 18</td>
</tr>
</tbody>
</table>

Table 5.20- Thorium (4$n$) series $\alpha$-particle spectrometry and ICP-MS results.

* $\pm 200\%$
<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Technique</th>
<th>Sand (Bq/kg) ($k=2$)</th>
<th>TiO$_2$ (Bq/kg) ($k=2$)</th>
<th>Tuff (Bq/kg) ($k=2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}$U</td>
<td>ICP-MS*</td>
<td>26 ± 1</td>
<td>6.2 ± 0.9</td>
<td>464 ± 10</td>
</tr>
<tr>
<td>$^{238}$U</td>
<td>$\alpha$-spectrometry</td>
<td>16 ± 1</td>
<td>13.0 ± 0.3</td>
<td>309 ± 15</td>
</tr>
<tr>
<td>$^{234}$U</td>
<td>$\alpha$-spectrometry</td>
<td>17 ± 2</td>
<td>15.7 ± 0.5</td>
<td>350 ± 17</td>
</tr>
<tr>
<td>$^{230}$Th</td>
<td>$\alpha$-spectrometry</td>
<td>11.2 ± 0.4</td>
<td>10.0 ± 0.5</td>
<td>231 ± 13</td>
</tr>
<tr>
<td>$^{210}$Po</td>
<td>$\alpha$-spectrometry</td>
<td>10 ± 1</td>
<td>65 ± 6</td>
<td>14 ± 2</td>
</tr>
</tbody>
</table>

Table 5.21- Uranium ($4n+2$) series $\alpha$-particle spectrometry and ICP-MS results.

* ± 200%

<table>
<thead>
<tr>
<th>Sample type</th>
<th>$^{236}$U Recovery (%)</th>
<th>$^{229}$Th Recovery (%)</th>
<th>$^{210}$Po Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>74%</td>
<td>65%</td>
<td>64%</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>72%</td>
<td>64%</td>
<td>68%</td>
</tr>
<tr>
<td>Tuff</td>
<td>82%</td>
<td>61%</td>
<td>60%</td>
</tr>
<tr>
<td>Reagent blank Th</td>
<td>-</td>
<td>67%</td>
<td></td>
</tr>
<tr>
<td>Reagent blank U</td>
<td>82%</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Reagent blank Po</td>
<td></td>
<td></td>
<td>70%</td>
</tr>
</tbody>
</table>

Table 5.22- Chemical recoveries based on $\alpha$-particle spectrometry measurements of U, Po and Th.
<table>
<thead>
<tr>
<th>Sample type</th>
<th>$^{236}\text{U}$ Recovery (%)</th>
<th>$^{239}\text{Th}$ Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>77 %</td>
<td>69%</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>79 %</td>
<td>66%</td>
</tr>
<tr>
<td>Tuff</td>
<td>73 %</td>
<td>60%</td>
</tr>
<tr>
<td>Reagent blank Th</td>
<td>-</td>
<td>72%</td>
</tr>
<tr>
<td>Reagent blank U</td>
<td>85 %</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.23- Chemical recoveries based on ICP-MS measurements of U and Th.
Figure 5.35- α-particle-spectra of Sand, TiO₂ and Tuff measured on Ortec Octete Plus NPL detectors 18, 19 for uranium and 20, 21 for thorium measurements respectively.
5.8.3 Reference material analysis

The activities gained from ICP-MS measurements are generally considerably higher than radiometric measurements; the reasons for this will be further explained in section 5.8.4.

$^{210}\text{Pb}$ results have been omitted as correction factors for self-attenuation result in the calibration factor varying by a factor of ~16 for the matrices considered (Landsberger and Millsap, 2014). In order to determine precise $^{210}\text{Pb}$ values further radiochemical analysis is recommended. Additionally, measurements of $^{210}\text{Po}$ seem to indicate chemical equilibrium between the preliminary $^{210}\text{Pb}$ and $^{210}\text{Po}$ in the Tuff and Sand material, but clear fractionation of $^{210}\text{Po}$ in the processed TiO$_2$ material. As discussed by Sethy, et al, (2015) the natural distribution of $^{210}\text{Po}$ in the environment is integrally dependant on that of its progenitor, $^{210}\text{Pb}$. With a half-life of 22.3 years (Kondev, 2008), ingrowth of $^{210}\text{Pb}$ is slow and its environmental transport largely controls the distribution of $^{210}\text{Po}$ (Vreček, et al, 2004). If $^{222}\text{Rn}$ decays in situ, then the chemistry of $^{210}\text{Pb}$ will largely control the fate of $^{210}\text{Po}$ subsequently produced. In environmental samples the $^{210}\text{Po}$ is often not in equilibrium with its $^{210}\text{Pb}$ parent (Sethy, et al, 2015). If the initial activity of $^{210}\text{Pb}$ is much higher than the activity of $^{210}\text{Po}$ as is found in the TiO$_2$ material. With a long-time period between sampling (2014) and Po separation (2016), the $^{210}\text{Po}$ activity changes considerably from its initial value at the sampling date due to the production of $^{210}\text{Po}$ from the $^{210}\text{Pb}$ decay and the decay of the $^{210}\text{Po}$ itself (Mathews, et al, 2007). This has to be considered in the calculation of decay correction of the $^{210}\text{Po}$ activity to the sampling date. Thus further analysis will be needed, to quantify the $^{210}\text{Pb}$ and $^{210}\text{Po}$, possibly using chemical separation of the isotopes and corresponding liquid scintillation analysis, by using counting windows to measure the activity of $^{210}\text{Bi}$ (Mathews, et al, 2007).

The radiometric results suggest that the Tuff is in near-equilibrium for both the $4n$ and $4n + 2$ decay series and there is reasonable consistency between the independent $\alpha$-particle and $\gamma$-ray
spectrometry measurements. This may be a result of the lack of processing of such material which, as stated above, is used directly as a building material.

Considering the Sand, the picture is somewhat different as both the $4n$ and $4n + 2$ series are in disequilibrium. Setting aside the ICP-MS data, the material appears to be slightly enriched in radium but depleted in thorium. This may be a consequence of the solubility of radium in water across a wide range of pH values, whereas thorium tends to only be soluble in low pH aqueous solvents. Furthermore, it may also be the case that the binding sites on sand preferentially adsorb radium. The activities and uncertainties of the $4n$ series in Sand are such that no firm conclusions can be drawn from this data.

For the TiO$_2$, it is clear that both the $4n$ and $4n + 2$ series are in disequilibrium, and it appears to be enriched in radium but depleted in thorium. This may be a consequence of the material processing, which is complex, and was not defined in detail by the supplier. However, it has been observed (Garcia-Tenorio, et al, 2013) that most of the radium remains associated with the undissolved material waste, with their work measuring radium activity concentrations into the kBq kg$^{-1}$ levels. The association of radium with undissolved waste is primarily a result of the digestion process of the ilmenite material with concentrated sulphuric acid, leading to precipitation of radium as radium sulphate (RaSO$_4$), the insolubility of which is well known (Landa, 2007).

The results for $^{228}$Th ($T_{1/2} = 1.91$ years) and its decay products are rather ambiguous. Although the levels of $^{228}$Ra ($T_{1/2} = 5.75$ years) and the $^{224}$Ra ($T_{1/2} = 3.66$ days) sub-series are similar (however the $^{224}$Ra sub-series is depleted with respect to $^{228}$Ra in Tuff) the activity
concentration of $^{228}\text{Th}$ determined by $\alpha$-particle spectrometry is rather low, from which, one might conclude, that there has been incomplete dissolution.

For the $4n + 2$ series, it is clear that $^{230}\text{Th}$ ($T_{1/2} = 7.54 \times 10^4$ years) years is depleted with respect to $^{226}\text{Ra}$ ($T_{1/2} = 1.6 \times 10^3$ years) even if the 5-6 times lower measurement of $^{228}\text{Th}$ by $\alpha$-particle spectrometry compared to $\gamma$-ray spectrometry is taken into account. This is particularly true for the Tuff and one may conclude that radium is more strongly bound than thorium to Tuff. However, it is difficult to resolve these observations without further experiments aimed at leaching (rather than fusion) the various matrices (Croudace, et al, 1998).

The measurement of NORM radionuclides in the three chosen standard reference materials has been undertaken. The dissolution process may not recover all of the thorium present in the samples and more work may be necessary to determine the levels of thorium isotopes with improved accuracy.

### 5.8.4 ICP-QQQ-MS calibration and validation

Unlike the procedures used for $\alpha$-spectrometry and $\gamma$-ray spectrometry, the procedures used for the ICP-MS measurements have not been validated according to ISO 17025. This is based on the fact that the instrument has only been recently installed at NPL, and that these forms of measurements have not been carried out on the instrument previously.

Calibration standards were prepared for $^{229}\text{Th}$, $^{232}\text{Th}$, $^{236}\text{U}$ and $^{238}\text{U}$ to determine instrument performance, limits of detection and to calculate recoveries. Over a period of time the instrument becomes less sensitive, thus reducing its detection of counts. As a result, internal
calibrations standards as seen in Figures 5.36 to 5.39 are used to apply drift corrections for any loss in signal. A series of analyte samples of different concentrations (e.g. concentration range 0.1 – 10 ppb) can be used to create calibration graphs which show a linear relation between the samples concentration and the CPS in the signal detected. It must be noted that the samples were not matrix matched for Tuff and TiO$_2$, as they underwent extensive chemical clean up, this was not deemed to be necessary.

The measurement time of all samples was approximately five minutes per sample, with the integrated autosampler enabling the elution fractions for Th and U in all matrices to be counted within one working day. The instrument backgrounds were counted before and after each sample, and background counts were subtracted. When running the blank samples (2 % HNO$_3$ (v/v)), the signal detected at an analytes mass is background noise, this is cumulative to the signal detected in an analyte sample. To prevent overestimating the concentration of the analyte in a specific sample, the background noise detected in the blank sample is subtracted from the total counts, this is known as blank correction.
Figure 5.36- Calibration graph for $^{229}$Th isotopes measured by ICP-MS*.

Figure 5.37- Calibration graph for $^{232}$Th isotopes measured by ICP-MS*.
*note much lower mass concentrations used in calibration samples than measured reference materials.

Based on the values derived in the calibration analysis, the ICP-MS standards used were up to three orders of magnitude less concentration of the radioisotopes of interest than the final analysed samples for $^{232}$Th and $^{238}$U (Table 5.24).
Especially in the Tuff sample, where the concentration of both uranium and thorium was significant higher than in the other two samples. It is estimated that this leads to an uncertainty in the extrapolated conversion between counts per second and activity concentration in the measured sample region by approximately a factor of three. Although it can be possible to dilute down the samples to the appropriate activity, this only yields an extra uncertainty and due to time constraints, this was not possible. Thus, this work allows for the potential of the NORM reference materials to act as calibration reference standards for future work in this field, for both higher activity measurements than the current reference standards used for calibration, but also for a variety of matrices.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sand $^{238}$U</th>
<th>$^{232}$Th</th>
<th>TiO$_2$ $^{238}$U</th>
<th>$^{232}$Th</th>
<th>Tuff $^{238}$U</th>
<th>$^{232}$Th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Concentration (ng/g)</td>
<td>9</td>
<td>1780</td>
<td>2</td>
<td>3860</td>
<td>160</td>
<td>120000</td>
</tr>
<tr>
<td>Activity Concentration (Bq/g)</td>
<td>0.026</td>
<td>0.007</td>
<td>0.006</td>
<td>0.012</td>
<td>0.464</td>
<td>0.484</td>
</tr>
</tbody>
</table>

Table 5.24- Th and U reference materials in terms of activity and mass concentration.

### 5.8.4.1 Detection limits ICP-MS measurement

Table 5.25 indicates the detection limits obtained by ICP-QQQ-MS, with a clear comparison with α-particle spectrometry, indicating much lower detection limits, in a much shorter sample measurement time.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$^{230}$Th</th>
<th>$^{232}$Th</th>
<th>$^{236}$U</th>
<th>$^{238}$U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counts per (pg/g)</td>
<td>1945</td>
<td>234</td>
<td>162</td>
<td>225</td>
</tr>
<tr>
<td>Limit of detection (pg/g)</td>
<td>2.0×10$^{-3}$</td>
<td>7.8×10$^{-3}$</td>
<td>7.8×10$^{-2}$</td>
<td>2.2</td>
</tr>
<tr>
<td>Limit of detection (Bq/g)</td>
<td>1.5×10$^{-5}$</td>
<td>3.1×10$^{-11}$</td>
<td>1.9×10$^{-3}$</td>
<td>2.7×10$^{-8}$</td>
</tr>
</tbody>
</table>

Table 5.25- Instrument detection limit for isotopes of Th and U using a blank sample composed of 1 gram of blank sand material spiked with each respective standard.
5.8.5 **Summary of results for the NORM Certified Reference Materials.**

The final certified values are all derived by the \( \gamma \)-ray and \( \alpha \)-spectrometry results such that they can be used to characterise these three materials making them suitable for use as certified reference standards for future measurement of NORM radionuclides with an uncertainty of \(<10\%\). The final NPL certified values for reference materials are outlined in Table 5.26:

Date of Calibration- 1 September 2016

Intended use- Calibration sources for \( \gamma \)-ray spectrometry measurements of NORM materials

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Technique</th>
<th>Sand (Bq/kg) ((k=2))</th>
<th>TiO(_2) (Bq/kg) ((k=2))</th>
<th>Tuff (Bq/kg) ((k=2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{238})U (via (^{234})Pa)</td>
<td>( \gamma )-spectrometry</td>
<td>(&lt;34)</td>
<td>(&lt;21)</td>
<td>(426 \pm 92)</td>
</tr>
<tr>
<td>(^{238})U</td>
<td>( \alpha )-spectrometry</td>
<td>(16 \pm 1)</td>
<td>(13.0 \pm 0.3)</td>
<td>(309 \pm 15)</td>
</tr>
<tr>
<td>(^{235})U</td>
<td>( \gamma )-spectrometry</td>
<td>(&lt;2)</td>
<td>(&lt;7)</td>
<td>(20 \pm 3)</td>
</tr>
<tr>
<td>(^{234})U</td>
<td>( \alpha )-spectrometry</td>
<td>(17 \pm 2)</td>
<td>(15.7 \pm 0.5)</td>
<td>(350 \pm 17)</td>
</tr>
<tr>
<td>(^{226})Ra (via (^{214})Pb and (^{214})Bi)</td>
<td>( \gamma )-spectrometry</td>
<td>(87 \pm 3)</td>
<td>(29,000 \pm 2,000)</td>
<td>(198 \pm 6)</td>
</tr>
<tr>
<td>(^{210})Po</td>
<td>( \alpha )-spectrometry</td>
<td>(10 \pm 1)</td>
<td>(65 \pm 6)</td>
<td>(14 \pm 2)</td>
</tr>
<tr>
<td>(^{232})Th (via (^{228})Ac, (^{212})Pb and (^{208})Tl)</td>
<td>( \gamma )-spectrometry</td>
<td>(7.0 \pm 0.7)</td>
<td>(19,600 \pm 1,300)</td>
<td>(354 \pm 24)</td>
</tr>
<tr>
<td>(^{228})Th</td>
<td>( \alpha )-spectrometry</td>
<td>(5.0 \pm 0.2)</td>
<td>(3430 \pm 110)</td>
<td>(321 \pm 18)</td>
</tr>
<tr>
<td>(^{230})Th</td>
<td>( \alpha )-spectrometry</td>
<td>(11.2 \pm 0.4)</td>
<td>(10.0 \pm 0.5)</td>
<td>(231 \pm 13)</td>
</tr>
</tbody>
</table>

Table 5.26- Final table of certified reference values for the NORM materials.

The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor \(k = 2\), providing a coverage probability of approximately 95\%. The uncertainty evaluation has been carried out in accordance with UKAS requirements.
Chapter 6

6. Production of Np-236 and chemical separation of fission fragments from $^{236}\text{Np}$ produced by proton irradiation of natural uranium target

6.1 General overview of chapter

This chapter will focus on the production of the radiotracer $^{236}\text{gNp}$ including the production mechanisms used involving charged-particle irradiation of uranium targets (specifically $\text{natU}$ but also $^{236}\text{U}$). As discussed briefly in Chapter 1 the ultimate aim of the current work is to develop and validate a radiochemical separation scheme capable of separating both $^{236}\text{gNp}$ and $^{236}\text{Pu}$ from a uranium target of natural isotopic composition (~1 g uranium) and ~200 MBq fission products. The chapter will focus on the results for the target and separated fractions which have been measured using ICP-MS as well as $\alpha$ and high-resolution $\gamma$-ray spectrometry to confirm the production and decay of $^{236}\text{Np}$ in either the ground state or metastable state. The mass distribution of the fission residues created during the target bombardment of natural uranium will also be presented and discussed.

6.2 Decay processes of $^{236}\text{Np}$

6.2.1 The low-lying structure of the odd-odd nucleus $^{236}\text{Np}$

The spin and parity of low-lying states in odd-odd nuclei (i.e., radionuclides with a single unpaired proton and neutron) are determined by the vector, angular momentum coupling of the two unpaired particles (Gallagher and Moszkowski, 1958).

The radionuclide $^{236}\text{gNp}$ is of interest both as a long-lived odd-odd isotope and as a chemical yield tracer. The parallel and antiparallel couplings of the final unpaired proton and neutron in this nucleus gives rise to two competing states with the same internal, single-particle configuration, which have assigned spin/parity $I^\pi = (6^-)$ and $(1^-)$ respectively. The higher-spin,
‘high-K’ coupling has been established as the ground state of this prolate deformed nucleus and decays with a half-life of $1.55(8) \times 10^5$ years (Chechev and Kuzmenko, 2012a). The antiparallel coupling of the Nilsson orbitals gives rise to the metastable, but considerably shorter-lived $I^p = K^\pi$ and $(1')$ state, which has an evaluated decay half-life of 22.5 h (Chechev and Kuzmenko, 2012b). Both of these states decay to excited states in $^{236}\text{U}$ (by electron capture) and $^{236}\text{Pu}$ (by $\beta^-$ decay) (Figure 6.1). The spin/parity of the decaying state has been established by the identification of electromagnetic transitions from high spin ($I^p = 6^+$) and low-spin ($I^p = 2^+$) states respectively which are populated in the daughter nuclei. The excitation energy difference between the $I^p = 6^-$ ground state and $I^p = 1$ excited state has not been established experimentally to date but evaluations suggest an energy difference of the order of 60 keV. This energy difference would give a direct measurement of the Nilsson orbital dependent proton-neutron residual interaction in this nucleus. The states populated following the decay of $^{236}\text{Np}$ are shown in Figure 6.1.
Figure 6.1 - $^{236}\text{Np}$ decay series populated following the decay of $^{236}\text{Np}$, note the 0.1% α-decay branch has yet to be observed.

Figure 6.2 - Neptunium-236g decay scheme.
The odd-odd nucleus $^{236}$Np has 93 protons and 143 neutrons and has an assigned ground state spin/parity of $I^\pi = (6^+)$. This is thought to arise from the maximum $K^\pi = 6^+$ projected angular-momentum coupling (where $K = \Omega_p + \Omega_n$) of the proton $[642]5/2^+\uparrow$ and neutron $[743]7/2^\uparrow$ Nilsson orbitals (Gorman and Asaro, 1970). In the Nilsson, orbital nomenclature $\Omega$, is the single-particle angular momentum of the unpaired particle and is equal to $\Delta \pm \Sigma$ where $\Delta$ is the orbital angular momentum projection on to the nuclear axis of symmetry and $\Sigma$ is the intrinsic nucleon spin $= \frac{1b}{2}$ (Walker and Dracoulis, 1999). The anti-parallel coupling of the same two orbitals $K = \Omega_p - \Omega_n = [5/2 - 7/2] = 1$ is thought to give the underlying structure of the first excited state of this nucleus (Browne and Tuli, 2006; Herzberg and Cox, 2011).

Although the relative excitation energy between the two couplings in $^{236}$Np has not been definitively determined, the most recent nuclear data evaluation for the $A = 236$ isobars suggests that the low-spin coupling lies approximately 60 keV above the long lived ground state. This is consistent with the expected Gallagher-Moszkowski coupling rules in deformed nuclei (Sood and Sheline, 1987).

The decay of the long-lived, high-spin coupling, ground state in $^{236}$Np ($^{236}$Np, $T_{1/2}$: 1.55(8) $\times$ 10$^5$ years, DDEP) proceeds by both $\beta^-$ decay to $^{236}$Pu and by electron capture to $^{236}$U (Browne and Tuli, 2006; Bé, et al, 2011) with a branching ratio of approximately 12.9% and 87.0% for the two branches respectively. The data used in this paper is from the data in DDEP, evaluated in 2009, and this half-life data is dependent on one source (Lindler, et al, 1981). The value quoted in ENSDF (1.53(5) $\times$ 10$^5$ years) is taken from an earlier evaluation (Browne and Tuli, 2006), which considers several published values. It is not clear why the later evaluation uses only the data from Lindler’s paper; in a recent review (Kellett, 2012) no additional requirement for half-life data was noted. The assigned spin and parity of the ground state for $^{236}$Np is consistent with the observed K-forbidden decays (Sood, et al, 2009) to the spin 6 ground-state
rotational band states, and their subsequent decay by characteristic E2 γ rays of energies 158.35 and 160.33 keV to $I^\pi = 4^+$ in the $^{236}\text{Pu}$ and $^{236}\text{U}$ daughter nuclei respectively (Ahmad, et al, 1983). There is also a small (<0.2%) α decay branch which has been inferred but not directly observed.

The first excited state in $^{236}\text{Np}$, is $^{236m}\text{Np}$, ($T_{1/2} = 22.5(4)$ hours; Chechev and Kuzmenko, 2012b) and, like the proposed $K^\pi = 6^-$ ground state, decays by $\beta^-$ and electron capture to $^{236}\text{Pu}$ and $^{236}\text{U}$ respectively. The branching ratio for the competing decay branches from the $^{236m}\text{Np}$ state are listed as 50(3)% for each decay mode in the most recent nuclear data sheets evaluation (Browne and Tuli, 2006). This majority of the decay strength from the $^{236m}\text{Np}$ state decays directly to the $0^+$ ground states and first $I^\pi = 2^+$ states in the $^{236}\text{Pu}$ and $^{236}\text{U}$ daughter nuclei, with a weak direct decay branch also identified the $K^\pi = 2^-$ excited state at 687.7 keV in $^{236}\text{U}$ (Lederer, et al, 1969). The electromagnetic (M5) direct decay branch from the $^{236m}\text{Np}$ (1-) metastable state to the proposed $K^\pi = 6^-$ $^{236}\text{Np}$ ground state has not been identified experimentally to date.

### 6.2.2 Formation of $^{236}\text{gNp}/^{236m}\text{Np}$

Neptunium-236g is usually accompanied by $^{236m}\text{Np}$, when produced using beam reactions and the production ratio between $^{236m}\text{Np}$ and $^{236}\text{gNp}$ is dependent on incoming particle energy, with lower ratios (i.e. favouring $^{236}\text{gNp}$ production) being favoured by higher incident particle energy (Aaltonen, et al, 1990). This is associated with the increased input angular momentum of the production reaction used for the production of $^{236}\text{Np}$ for higher beam energies. For production using the $^{238}\text{U}(p,3n)^{236}\text{Np}$ reaction, the increase in production ratios between the $^{236m}\text{Np}$ and $^{236}\text{Np}$ has been shown to increase systematically with increasing input angular momentum and thus beam energy (Figure 6.3) (Aaltonen, et al, 1990), with a ratio of close to
unity estimated for input angular momenta of >15 h. The decay of $^{236\text{g}}\text{Np}$ generates a number of β-particles and γ rays (Chechev and Kuzmenko, 2009) and are detailed in Table 6.1.

<table>
<thead>
<tr>
<th>Neptunium-236g</th>
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<tbody>
<tr>
<td>Half life</td>
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<tr>
<td>Decay transitions</td>
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<td>Energy (keV)</td>
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<td>B (End points from Qβ⁻)</td>
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<td>Electron capture</td>
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Table 6.1- $^{236\text{g}}\text{Np}$ decay data (Chechev and Kuzmenko, 2012).

When considering the production of $^{236}\text{Np}$, the formation ratio of $^{236\text{m}}\text{Np}$ to $^{236\text{g}}\text{Np}$ must also be considered. This is not well established and is also likely to be production-reaction dependent, but has been estimated to range between a factor of one to six in previous literature (Figure 6.3) (Aaltonen, et al, 1990; Efurd, et al, 1991; Gindler and Sjoblom, 1959) in favour of the high-spin ground state. This is likely to be of this order or even larger with the use of a fusion-evaporation reaction which are well known to preferentially populate near-yrast, high-spin states in the residual decay. This can be used to estimate the total amount of $^{236}\text{Np}$ tracer that was created in the target irradiation and available for extraction and measurement of the
characteristic decay properties. Following different chemical separations to attempt to preferentially select the $^{236}\text{Np}$ tracer from other decay products, target material and fission decay products, which were also produced in significant quantities in the target irradiation following the proton-induced fission of $^{238}\text{U}$ (Larijani, et al, 2015).

![Graph showing the formation ratio between $^{236}\text{gNp}$ and $^{236}\text{mNp}$ in the $^{238}\text{U(p,3n)}^{236}\text{Np}$ reaction as reported by Aaltonen, et al, (1990).](image)

**Figure 6.3-** Formation ratio between $^{236}\text{gNp}$ and $^{236}\text{mNp}$ in the $^{238}\text{U(p,3n)}^{236}\text{Np}$ reaction as reported by Aaltonen, et al, (1990).

### 6.2.3 Previous methods of Np production

The irradiation of uranium with charged particles has been studied by a number of groups worldwide, including in the USA, UK, Finland, Russia and Japan. These groups have generated data on cross sections, although when the results are compared, there are a number of inconsistencies. Since natural uranium; high-enrichment $^{235}\text{U}$ and high-enrichment $^{236}\text{U}$ are the
only potential target materials available to NPL, only proton and deuteron irradiation of these isotopes were considered further. The possible routes to production of $^{236}$Np are set out in Jerome, et al, 2014, however the focus of this work is based on the $^{238}$U$(p,3n)^{236}$Np fusion-evaporation reaction (a literature study of the other possible reactions can be found in Appendix G).

6.2.3.1 Uranium-238 irradiations

Several groups have irradiated $^{238}$U with protons (Aaltonen et al, 1990; Aaltonen et al, 1994; Ageev et al, 1987; Bellido et al, 1994; Guzhovskii et al, 1994; Zhao et al, 1999). None provide experimental data concerning the formation of $^{237}$Np, although Bellido et al, (1994) carry out an estimation of this cross-section, based on an optical model, predicting that the cross section for $^{237}$Np formation peaks at around 12-15 MeV. The published data is shown in Figure 6.4 and indicates reasonable consistency between the various data sets.

There is some data to suggest that $^{237m}$Np is formed by the $(p,2n)$ reaction, although the cross sections are $<10^{-6}$ barns (Migneco et al, 1977). We can note from this plot that the optimum proton beam energy window for $^{236}$Np formation is ~15-30 MeV, and that for $^{235}$Np is ~25-40 MeV.

The excitation energy study by Aaltonen et al, (1990) using the $^{238}$U$(p,3n)^{236}$Np fusion-evaporation reaction shows the maximum production cross-section for both the long-lived ($I^\pi=6^-$) and short-lived ($I^\pi=1^+$) decaying states in $^{236}$Np reach a maximum at a beam energy of approximately 21 MeV. The ratio of high-spin (ground state) to low-spin ($^{236m}$Np) state production was found to increase with increasing beam energy, with the production of $^{236g}$Np levelling out at constant value of approximately 10 mb for beam energies between 20 and 28
MeV. The measured production cross-section for the shorter-lived $1^-$ isomeric state drops by a factor of approximately three over the same beam energy range (Aaltonen, \textit{et al}, 1990).

Figure 6.4- Summary of published cross sections for the $^{238}\text{U}(p,xn)^{(239-x)}\text{Np}$ reactions.
6.2.4 Estimate of the initial $^{236}$Np production yield for the $^{238}$U($p,3n$)$^{236}$Np reaction

A target containing 1.2 g of UO$_2$ was irradiated with a beam of 25 MeV protons of typical beam current of 30 μA at the University of Birmingham cyclotron facility. The target was produced by compacting natural uranium dioxide at 60 kN.cm$^{-2}$ between an aluminium target holder and a 0.025 mm titanium foil, then subjected to a proton irradiation for a total duration of 19 hours over a period of three days (9–11$^{th}$ December 2013).

The estimated production of $^{236}$Np in the current study can be determined using the production relation:

$$R = \sigma \cdot \varphi \cdot n \quad (Equation \ 6.1)$$

where:

- $R$: is number of $^{236}$Np atoms formed per second per unit volume (units s$^{-1}$ cm$^{-3}$)
- $\sigma$: is the production cross section (units in cm$^2$, where 1 b = 10$^{-24}$ cm$^2$)
- $\varphi$: is the particle flux per unit area (cm$^2$ s$^{-1}$)
- $n$: is the number of target atoms per unit volume (cm$^{-3}$)

The particle flux per unit area is not known in detail since the cross-section of the beam was not well established, however, since the stated beam current was delivered to the entire target, then we can assume:

$$P_{tot} = \sigma \cdot \varphi_{tot} \cdot n_{tot} \cdot t \quad (Equation \ 6.2)$$
where:

$P_{tot}$: total number of product atoms ($^{236}$Np) formed and

$\varphi_{tot}$: total particle flux ($s^{-1}$), where:

$$\varphi_{tot} = \frac{l}{e} \quad (Equation \ 6.3)$$

$I$: beam current (A)

e: fundamental electrical charge (A.s)

$n_{tot}$: total number of target atoms irradiated (dimensionless), where:

$$n_{tot} = \frac{m_t N_a M_r}{M} f_i \quad (Equation \ 6.4)$$

$m_t$: mass of the target in g

$M_r$: relative molecular mass of the target compound (g.mol$^{-1}$)

$M$: mols of the element of interest per mole of the target compound (dimensionless)

$f_i$: abundance of the isotope of interest in that element (dimensionless)

$N_a$: Avogadro constant (mol$^{-1}$)

$t$: irradiation time (s)

Thus we obtain the relation for the total number of produced $^{236}$Np atoms (neglecting any decay during the irradiation period) of:

$$P_{tot} = \sigma \left(\frac{l}{e}\right) \left(\frac{m_t N_a M_r f_i}{M}ight) t \quad (Equation \ 6.5)$$

where for this particular production experimental production run;

$\sigma \approx 53 \times 10^{-27} \ cm^2$ is the estimated production cross-section of $^{236}$Np via the $^{238}$U($p,3n$)$^{236}$Np nuclear reaction (using the PACE IV fusion evaporation code) and $I \approx 30 \times 10^{-6} \ A.$
This leads to a value of:

\[ \varphi_{tot} = \frac{30 \times 10^{-6}}{1.602 \times 10^{-19}} \approx 1.9 \times 10^{14} \text{ s}^{-1} \ (Equation \ 6.6) \]

Also:

\[ m_t \approx 1.2 \text{ g of UO}_2 \text{ in the production target} \]

\[ M_r = 270.03 \text{ g mol}^{-1} \]

\[ M = 1 \]

\[ f_i = 0.9928, \text{ and} \]

\[ N_a = 6.022 \times 10^{23} \text{ mol}^{-1}, \text{ so} \]

\[ n_{tot} = \frac{1.2 \times 6.022 \times 10^{23} \times 1 \times 0.9928}{270.03} \approx 2.7 \times 10^{21} \ (Equation \ 6.7) \]

\[ t = 18.75 \text{ h} = 67500 \text{ s} = \text{ the total irradiation time.} \]

This leads to an (upper limit) estimate of the total production of \(^{236}\text{Np}\) (i.e. in both the ground and metastable states) in this experiment of approximately \(1.7 \times 10^{15}\) atoms, which is equivalent to a \(^{236}\text{Np}\) mass of approximately \(7 \times 10^{-7}\) g = 700 ng.

This number of atoms would result in a maximum value for the activity of \(^{236}\text{Np}\) \((t_p = 1.55 \times 10^5 \text{ y} = 4.891 \times 10^{12} \text{ s})\) which is approximately 350 Bq. When considering the production of \(^{236}\text{Np}\), the formation ratio of \(^{236m}\text{Np}\) to \(^{236g}\text{Np}\) must also be considered. This is not well established and is also likely to be production-reaction dependent, but has been estimated to be factor of one to six in previous literature (Aaltonen, *et al*, 1990; Efurd, *et al*, 1990; Efurd, *et al*, 1990).
1991; Gindler and Sjoblom, 1959) in favour of the high-spin ground state. Therefore, the predicted amount of \(^{236}\text{Np}\) formed is \(~99 \times 10^{-9}\) g \(\equiv \sim 36\) Bq. The factor is likely to be of this order or even larger with the use of a fusion-evaporation reaction which are well known to preferentially populate near-yrast, high-spin states in the residual decay. This gives a useful estimate of the total amount of \(^{236}\text{Np}\) tracer that was created in the target irradiation, and available for extraction and measurement of the characteristic decay properties. Following different chemical separations to attempt to preferentially select the \(^{236}\text{Np}\) tracer from the fission decay products, which were also produced in significant quantities in the target irradiation following the proton-induced fission of \(^{238}\text{U}\) (Larijani, et al, 2015).

6.2.5 Target preparation, irradiation and processing

6.2.5.1 Target considerations

According to Stolarz, (2014) in nuclear physics a target can be defined as ‘an object or system subjected to bombardment by particles such as electrons, protons, etc., or to radiation’ the success of any irradiation is largely dependent on the target considerations. The requested target thickness should (in most cases) be uniform and have good mechanical strength and stability under beam irradiation, as well as high chemical purity and isotopic purity. A high thickness of the targets is required to assure the best possible yield of isotopes production but they also have to be robust to sustain the energy deposited in the target by very intensive beams. The target produced in this work was compacted at 60 kN/cm\(^2\) between an aluminium target holder, 0.025 mm titanium foil and featured approximately 500 mg/cm\(^2\) of uranium target material.

Due to the relatively low cost of \(^{\text{nat}}\text{U}\) and there being no requirement for the material to be recovered, it was decided that all initial tests of target substrate material and preparation would be carried out on natural uranium targets which are essentially isotopically pure (99.7\% \(^{238}\text{U}\)).
In the initial target production procedure, metallic uranium was used as the target material, however it was found that metallic uranium rapidly oxidised during the irradiation, thus caught fire and was not deemed to be suitable.

![Image of initial target](image)

Figure 6.5- Initial target made up of metallic uranium which was oxidised during the irradiation and caught fire in the Birmingham Cyclotron.

It is imperative not to produce uranyl nitrate hexahydrate (UO$_2$(NO$_3$)$_2$), as the reaction leads to flakes of uranium expanding from the target, although soluble in ethanol and acetone, it is best avoided. It was decided that the relatively stable compound uranium oxide (UO$_2$) converted from nitrate was the optimum compound used in the reaction.
The following figure is a schematic in photographic form of the final target production procedure:

Figure 6.6- Schematic of the four stages of the target production process:

1. Uranium being converted into oxide form (top left)
2. UO₂ placed in target (top right)
3. Target covered with 0.025 mm titanium foil before sent for irradiation (bottom left)
4. Target one month after irradiation (bottom right)

6.2.5.2 Irradiation facility University of Birmingham Nuclear Physics Research Group Cyclotron

The Scanditronix MC40 cyclotron transferred from Minneapolis to Birmingham in 2002 and commissioned in the Physics group in 2004 (Marin-Reyes, et al, 2002; Parker, et al, 2002),
being used primarily as a means to produce radioisotopes for both medical imaging, and for the production of proton rich radionuclides supporting a wide range of radiochemical analyses via radioactive yield tracers such as $^{95m}$Tc (Jerome, et al, 2012).

The cyclotron is a particle accelerator in which ions are accelerated as they orbit in a magnetic field. The Birmingham Cyclotron can accelerate ions within the following energy ranges (Parker, et al, 2002):

- Proton beam: $\leq 9$ and $12 – 39$ MeV
- Deuteron beam: $6 – 19.5$ MeV
- $^3$He beam: $\leq 27$ and $36 – 54$ MeV
- $\alpha$ beam: $12 – 39$ MeV

Figure 6.7- Photograph of the University of Birmingham Cyclotron.
6.2.5.3 Initial processing of targets before radiochemical analysis

NPL does not have a hot cell facility, thus the irradiated target was handled in standard fume cupboards, with appropriate lead shielding. In respect of this the target was left to cool for a period of one month, in order for the short lived fission products to decay and to allow for the safe handling.

A glove box was set up to process the target, this was done to ensure no contamination was spread, the target was transferred to the glove box and opened. Once opened the target was dissolved in 8 M nitric acid into two separate centrifuge tube, to make sure all the target material was dissolved and as little residue material was put to waste as possible. The material was then transferred into two bottles, to make sure all the residue target material was dissolved, to be then chemically separated to isolate the produced Np. The work carried out on the
measurement of the fission fragment residues was from a 1ml aliquot taken from the natU target as soon it was dissolved as shown in Figure 6.9.

![Figure 6.9- Target material dissolved into 8 M HNO₃.](image)

### 6.2.6 Validation work to select reducing agent

Although the neptunyl ion is similar to the uranyl ion, it requires forcing conditions, as previously mentioned the Np⁵⁺ is not extracted into diethyl ether due to the complications by the instability of Np⁴⁺ in nitric acid, thus it is necessary to force reduction of Np⁵⁺ to Np⁴⁺. Many approaches are possible – NO₂⁻, hydroxylamine, ferrous sulphamate, ascorbic acid and ferric ion.

In order to select the optimum reducing agent for Np a study was carried out looking at the redox behaviour of Np. The study aimed to determine Np sorption on both TEVA resins before being adopted on the irradiated material.
The validation work was conducted on \(^{239}\text{Np}\), which was chemically separated from \(^{243}\text{Am}\). The separated \(^{239}\text{Np}\) was measured on ‘Lancelot’ and split into three fractions, dissolved in 10 mL of:

1. \(2.5 \text{ M } \text{HNO}_3 + 0.1 \text{ M } \text{NaNO}_2\)
2. \(2.5 \text{ M } \text{HNO}_3 + 1.25 \text{ mL of } 1.5 \text{ M ascorbic acid}\)
3. \(2.5 \text{ M } \text{HNO}_3 + 0.5 \text{ mL of } 1.5 \text{ M sulfamic acid}\)

1 mL of each fraction was measured on ‘Lancelot’ and then loaded on the three TEVA columns, which were all pre-treated with 10 mL 2.5 M HNO\(_3\). The column was then rinsed with another 10 mL of the loading solution and the contents of the separation was collected and measured again. Where redox control has worked, we would expect to see no Np in the rinsing solution as Np(IV) is completely sorbed on the resin. The study showed the following results:

<table>
<thead>
<tr>
<th>Method Description</th>
<th>Result</th>
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<tbody>
<tr>
<td>(2.5 \text{ M } \text{HNO}_3 + 0.1 \text{ M } \text{NaNO}_2)</td>
<td>Strange blue colour in column and 13% of initial Np found in rinse.</td>
</tr>
<tr>
<td>(2.5 \text{ M } \text{HNO}_3 + 1.25 \text{ mL of } 1.5 \text{ M ascorbic acid})</td>
<td>Method worked no Np in final fraction</td>
</tr>
<tr>
<td>(2.5 \text{ M } \text{HNO}_3 + 0.5 \text{ mL of } 1.5 \text{ M sulfamic acid})</td>
<td>Method worked trace amounts of Np in final fraction &lt;5%</td>
</tr>
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</table>

Table 6.2- Summary of results from reducing agent selection.

The next step using the TEVA method was to strip Np using 20 mL 0.2 M HNO\(_3\). This was measured again on ‘Lancelot’ and no Np was recovered. Looking at previous sorption studies this was slightly unexpected, and consequently 0.1 M HNO\(_3\) was used which proved successful. Here Np was seen in the fractions, and the recoveries of both the ascorbic acid and sulfamic acid were similar and notably greater than using NaNO\(_2\). Another key factor was the
significantly longer elution time using the NaNO$_2$ method, the solution used in the initial steps was made fresh, and was well shaken. However its effects on the TEVA resin were clear to see in the distinct change in colour of the column, which turned pale blue. Thus based on the validation work, Fe$^{3+}$ with ascorbic acid was selected, as the Ascorbic acid reduces Fe$^{3+}$ to Fe$^{2+}$ and thus the Fe$^{2+}$ reduces Np$^{5+}$ to Np$^{4+}$ and allows the Np to be adsorbed onto the resin. Thus the oxidation state of neptunium was fixed to Np(IV) with the addition of 1.2 mg/g Fe$^{3+}$ and 150 mg/g ascorbic acid (Strišovská, et al, 2013) before loading on TEVA column from 2.5 M HNO$_3$ to separate $^{236}$Np and $^{236}$Pu from the fission products. Both Np(IV) and Pu(IV) are strongly retained by the TEVA resin with distribution coefficients of $K_d = 5 \cdot 10^3$ for Np(IV) and $K_d = 3 \cdot 10^4$ in case of Pu(IV) (Horwitz, et al, 1995). No significant retention of the major fission products by TEVA resin from 2.5 M HNO$_3$ was observed during the method validation work, therefore the fission products have been removed from the column by rinse with 20 mL of 2.5 M HNO$_3$ solution.

6.2.7 Radiochemical Separation procedure for Np isolation

The proposed separation procedure for $^{236}$Np from an irradiated target can be divided into three stages;

- **Removal of the target matrix, UO$_2$:**

  This was achieved by dissolution of uranium in nitric acid, followed by extraction of uranium into diethyl ether (Furman, *et al*, 1955); diethyl ether specifically extracts uranium from nitric acid solutions, leaving all other elements in the aqueous phase, due to the octahedral complex and polarity of PuO$_2^{2+}$ and NpO$_2^{2+}$ they do not bind with the C$_2$H$_5$OC$_2$H$_5$, as the surrounding negative charge of the atoms repels oxygen. Thus the PuO$_2^{2+}$ and NpO$_2^{2+}$ are not compatible with ether extraction. Although there is a limited
solubility of the aqueous phase in the ether phase and *vice versa*, necessitating additional extractions.

- **Isolation of neptunium:**

  Although neptunium displays a number of oxidation states, the Np$^{4+}$ ion is not stable in acid solution and may be oxidised to Np$^{5+}$ in the presence of nitric acid. However, the Np$^{4+}$ ion is retained by TEVA extraction chromatography resin (Horwitz, *et al.*, 1995); in 2.5 M HNO$_3$, the Np$^{4+}$ ion has a distribution coefficient ($k_d$) of ~ 5,000 and may be stabilised by reduction with ascorbic acid in the presence of the ferric ion, Fe$^{3+}$ (Strišovská, *et al.*, 2013). Under the same conditions, the $k_d$ for Pu$^{4+}$ is ~30,000. No significant retention of the major fission products by TEVA resin from 2.5 M HNO$_3$ was observed during the method validation work. Therefore the fission products have been removed from the column by rinse with 20 mL of 2.5 M nitric acid solution as shown in Figure 6.10. However, the very high levels of fission products > 50 MBq, depending on cooling time, necessitate additional clean-up of the separated neptunium.

- **Isolation of plutonium**

  Furthermore, it is possible to selectively elute $^{236}$Pu from the TEVA resin by reduction of Pu$^{4+}$ to Pu$^{3+}$ by rinsing the column with 20 mL of 9 M HCl containing 0.1 M of NH$_4$I prior to stripping $^{236}$Np by washing with 10 mL of 0.1 M HCl (Figure 6.10).

Prior to testing with the target material, the procedures were tested for a simulated fission product solution using stable element standards (Zr, Nb, Mo, Ru, Ba, La, Ce, Sb), with recoveries from each stage assessed by ICP-MS.
Figure 6.10- Schematic view of the separation procedure used to isolate $^{236}\text{Np}$ and $^{236}\text{Pu}$ from the irradiated target solution.

6.2.8 Instrumentation

6.2.8.1 Gamma-Ray Spectrometry

Three different HPGe $\gamma$-ray spectrometers were used for the work carried out in this chapter: ‘Lancelot’ (as described previously in Chapter 5), ‘Bart’ and ‘Sir Robin’ which is a high efficiency well detector.

6.2.8.1.1 Bart

Gamma-ray spectrometry analysis of the fission fragments was carried out on the p-type detector ‘Bart’ (for photograph of detector see Appendix E) with a beryllium window and a relative efficiency of 28.9% and energy resolution of 1.78 keV at 1.33 MeV using $^{60}\text{Co}$ was used to measure the solution dispensed into the BS ampoule (Collins, et al, 2014). The detector used a graded shield of Pb, Cd and Cu and utilised identical electronic set-ups, incorporating a Canberra AFT research amplifier (6 $\mu$s shaping time) and utilising the “PUR/DT” circuitry to
correct the Live Time for pile-up and dead time (Collins, *et al.*, 2014). Energy calibration of the detector was carried out using a $^{152}$Eu source with peak centroids set within 0.1 keV for $\gamma$ emissions with intensities in excess of 1% using the evaluated energies from the Decay Data Evaluation Project. The efficiency calibration for ‘Bart’ was carried out using the standard NPL Mix R08-03, which is $^{241}$Am, $^{109}$Cd, $^{57}$Co, $^{139}$Ce, $^{51}$Cr, $^{113}$Sn, $^{85}$Sr, $^{137}$Cs, $^{54}$Mn, $^{88}$Y, $^{65}$Zn and $^{60}$Co in 4 M HCl. In addition to these radionuclides additional calibration points were added using solutions of single radionuclides of $^{51}$Cr, $^{75}$Se, $^{85}$Sr, $^{109}$Cd, $^{125}$I, $^{141}$Ce and $^{210}$Pb, where the individual radionuclides had been standardised at NPL using the NPL re-entrant Ionisation Chamber which is directly traceable to primary standards. The specific count rate per gram in the major full-energy peaks were calculated for each measurement, correcting for radioactive decay, dead time and density and the results combined as the arithmetic mean. Each calibration sample was in a matched geometry for the measurement samples, which was 2 mL glass BS ampoule at 30 cm (marked distance 3) from the detector window, for a live time of 50,000 seconds. The measurements were taken at 30 cm in order to cover a solid angle of 0.45 sr from the source and to thus reduce the effects of pileup on the detector. Measurements were taken for a duration of 8 months (from February to September, 2014) throughout the project to obtain the dataset that was analysed in the current work.

<table>
<thead>
<tr>
<th>Detector model</th>
<th>GMX-25190-P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Serial number</td>
<td>39-TN21336A</td>
</tr>
<tr>
<td>Diameter</td>
<td>55.2mm</td>
</tr>
<tr>
<td>Length</td>
<td>57.0mm</td>
</tr>
<tr>
<td>End cap to detector</td>
<td>3mm</td>
</tr>
<tr>
<td>Bias Voltage (V dc)</td>
<td>+2700</td>
</tr>
</tbody>
</table>

Table 6.3- Detector characteristics of ‘Bart’.
<table>
<thead>
<tr>
<th>Energy /keV</th>
<th>Radionuclide</th>
<th>Full energy peak detection efficiency</th>
<th>Expanded Uncertainty ($k = 2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.41295</td>
<td>$^{57}$Co</td>
<td>$2.46 \times 10^{-4}$</td>
<td>$\pm 0.10 \times 10^{-4}$ (± 4.4 %)</td>
</tr>
<tr>
<td>26.3446 (4)</td>
<td>$^{241}$Am</td>
<td>$1.27 \times 10^{-3}$</td>
<td>$\pm 0.10 \times 10^{-3}$ (± 8 %)</td>
</tr>
<tr>
<td>35.4922</td>
<td>$^{125}$I</td>
<td>$1.52 \times 10^{-3}$</td>
<td>$\pm 0.08 \times 10^{-3}$ (± 4.4 %)</td>
</tr>
<tr>
<td>46.539</td>
<td>$^{210}$Pb</td>
<td>$1.648 \times 10^{-3}$</td>
<td>$\pm 0.046 \times 10^{-3}$ (± 2.8 %)</td>
</tr>
<tr>
<td>59.5409 (2)</td>
<td>$^{241}$Am</td>
<td>$1.668 \times 10^{-3}$</td>
<td>$\pm 0.020 \times 10^{-3}$ (± 1.2 %)</td>
</tr>
<tr>
<td>66.0518</td>
<td>$^{75}$Se</td>
<td>$1.684 \times 10^{-3}$</td>
<td>$\pm 0.044 \times 10^{-3}$ (± 2.6 %)</td>
</tr>
<tr>
<td>88.0336 (2)</td>
<td>$^{109}$Cd</td>
<td>$1.668 \times 10^{-3}$</td>
<td>$\pm 0.044 \times 10^{-3}$ (± 2.6 %)</td>
</tr>
<tr>
<td>96.734</td>
<td>$^{75}$Se</td>
<td>$1.655 \times 10^{-3}$</td>
<td>$\pm 0.038 \times 10^{-3}$ (± 2.2 %)</td>
</tr>
<tr>
<td>121.1155</td>
<td>$^{75}$Se</td>
<td>$1.594 \times 10^{-3}$</td>
<td>$\pm 0.036 \times 10^{-3}$ (± 2.2 %)</td>
</tr>
<tr>
<td>122.06065 (24)</td>
<td>$^{57}$Co</td>
<td>$1.601 \times 10^{-3}$</td>
<td>$\pm 0.022 \times 10^{-3}$ (± 1.4 %)</td>
</tr>
<tr>
<td>136.0001</td>
<td>$^{75}$Se</td>
<td>$1.540 \times 10^{-3}$</td>
<td>$\pm 0.034 \times 10^{-3}$ (± 2.2 %)</td>
</tr>
<tr>
<td>136.47356</td>
<td>$^{57}$Co</td>
<td>$1.537 \times 10^{-3}$</td>
<td>$\pm 0.048 \times 10^{-3}$ (± 3.2 %)</td>
</tr>
<tr>
<td>165.8575 (22)</td>
<td>$^{139}$Ce</td>
<td>$1.415 \times 10^{-3}$</td>
<td>$\pm 0.044 \times 10^{-3}$ (± 3 %)</td>
</tr>
<tr>
<td>198.606</td>
<td>$^{75}$Se</td>
<td>$1.258 \times 10^{-3}$</td>
<td>$\pm 0.030 \times 10^{-3}$ (± 2.4 %)</td>
</tr>
<tr>
<td>264.6576</td>
<td>$^{75}$Se</td>
<td>$1.004 \times 10^{-3}$</td>
<td>$\pm 0.022 \times 10^{-3}$ (± 2.2 %)</td>
</tr>
<tr>
<td>279.5422</td>
<td>$^{75}$Se</td>
<td>$9.59 \times 10^{-4}$</td>
<td>$\pm 0.020 \times 10^{-4}$ (± 2.0 %)</td>
</tr>
<tr>
<td>303.9236</td>
<td>$^{75}$Se</td>
<td>$8.97 \times 10^{-4}$</td>
<td>$\pm 0.020 \times 10^{-4}$ (± 2.2 %)</td>
</tr>
<tr>
<td>320.0835 (8)</td>
<td>$^{51}$Cr</td>
<td>$8.55 \times 10^{-4}$</td>
<td>$\pm 0.016 \times 10^{-4}$ (± 1.8 %)</td>
</tr>
<tr>
<td>391.698 (6)</td>
<td>$^{113}$Sn</td>
<td>$7.15 \times 10^{-4}$</td>
<td>$\pm 0.012 \times 10^{-4}$ (± 1.6 %)</td>
</tr>
<tr>
<td>400.6572</td>
<td>$^{75}$Se</td>
<td>$7.06 \times 10^{-4}$</td>
<td>$\pm 0.016 \times 10^{-4}$ (± 2.2 %)</td>
</tr>
<tr>
<td>514.0048 (44)</td>
<td>$^{85}$Sr</td>
<td>$5.62 \times 10^{-4}$</td>
<td>$\pm 0.010 \times 10^{-4}$ (± 1.6 %)</td>
</tr>
<tr>
<td>661.657 (6)</td>
<td>$^{137}$Cs</td>
<td>$4.52 \times 10^{-4}$</td>
<td>$\pm 0.010 \times 10^{-4}$ (± 2.0 %)</td>
</tr>
<tr>
<td>834.838 (10)</td>
<td>$^{58}$Mn</td>
<td>$3.71 \times 10^{-4}$</td>
<td>$\pm 0.006 \times 10^{-4}$ (± 1.4 %)</td>
</tr>
<tr>
<td>898.036 (8)</td>
<td>$^{88}$Y</td>
<td>$3.488 \times 10^{-4}$</td>
<td>$\pm 0.0048 \times 10^{-4}$ (± 1.4 %)</td>
</tr>
<tr>
<td>1115.539 (4)</td>
<td>$^{65}$Zn</td>
<td>$2.92 \times 10^{-4}$</td>
<td>$\pm 0.0006 \times 10^{-4}$ (± 1.8 %)</td>
</tr>
<tr>
<td>1173.228 (6)</td>
<td>$^{60}$Co</td>
<td>$2.81 \times 10^{-4}$</td>
<td>$\pm 0.00006 \times 10^{-4}$ (± 2.2 %)</td>
</tr>
<tr>
<td>1332.492 (8)</td>
<td>$^{60}$Co</td>
<td>$2.516 \times 10^{-4}$</td>
<td>$\pm 0.00042 \times 10^{-4}$ (± 1.6 %)</td>
</tr>
<tr>
<td>1836.052 (26)</td>
<td>$^{88}$Y</td>
<td>$1.908 \times 10^{-4}$</td>
<td>$\pm 0.00048 \times 10^{-4}$ (± 2.4 %)</td>
</tr>
</tbody>
</table>

Table 6.4- Efficiency calibration data for ‘Bart’, gamma emission energies and gamma emission data of the radionuclides are taken from the evaluations of the Decay Data Evaluation
Project, www.nucleide.org/DDEP.htm. The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95%. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

![Figure 6.11- Efficiency response of ‘Bart’ shown on linear scale at different γ-ray energy using the NPL standard mix source R08-03, and additional calibration points were added using solutions of single radionuclides of $^{51}$Cr, $^{75}$Se, $^{85}$Sr, $^{109}$Cd, $^{125}$I, $^{141}$Ce and $^{210}$Pb.]

6.2.8.1.2 Sir Robin

Sir Robin a well detector (for photograph of detector see Appendix E) was used to measure the $^{236}$Np fraction, samples were mounted directly in the aluminium-lined rentrant well of the detector, with no sample holder. The detector was calibrated using a series of standards of $^{210}$Pb, $^{109}$Cd, $^{75}$Se, $^{57}$Co, $^{141}$Ce, $^{75}$Se, $^{51}$Cr, $^{137}$Cs and $^{54}$Mn, full energy peak efficiencies were determined using γ-ray emissions not significantly affected by coincidence summing.
Detector model | GWL-250240-S
---|---
Serial number | 38-P21333A
Diameter | 54.2 mm
Length | 56.0 mm
End cap to detector | 3 mm
Bias Voltage (V dc) | + 2700

Table 6.5- Detector characteristics of ‘Sir Robin’.

<table>
<thead>
<tr>
<th>Gamma Emission Energy /keV</th>
<th>Radionuclide</th>
<th>Full energy peak detection efficiency</th>
<th>Expanded Uncertainty ($k = 2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>46.539 ± 0.002</td>
<td>$^{210}$Pb</td>
<td>0.0489</td>
<td>± 0.014 (± 2.8%)</td>
</tr>
<tr>
<td>88.0336 ± 0.0002</td>
<td>$^{109}$Cd</td>
<td>0.575</td>
<td>± 0.014 (2.4%)</td>
</tr>
<tr>
<td>96.7340 ± 0.0018</td>
<td>$^{75}$Se</td>
<td>0.615</td>
<td>± 0.024 (± 3.8%)</td>
</tr>
<tr>
<td>136.47356 ± 0.00024</td>
<td>$^{57}$Co</td>
<td>0.537</td>
<td>± 0.018 (± 3.2%)</td>
</tr>
<tr>
<td>145.4433 ± 0.0028</td>
<td>$^{141}$Ce</td>
<td>0.519</td>
<td>± 0.012 (± 2.4%)</td>
</tr>
<tr>
<td>303.9236 ± 0.0020</td>
<td>$^{75}$Se</td>
<td>0.281</td>
<td>± 0.012 (± 3.8%)</td>
</tr>
<tr>
<td>320.0835 ± 0.0008</td>
<td>$^{51}$Cr</td>
<td>0.27788</td>
<td>± 0.0050 (± 1.8%)</td>
</tr>
<tr>
<td>661.657 ± 0.006</td>
<td>$^{137}$Cs</td>
<td>0.1475</td>
<td>± 0.0024 (± 1.6%)</td>
</tr>
<tr>
<td>834.838 ± 0.010</td>
<td>$^{54}$Mn</td>
<td>0.1182</td>
<td>± 0.0012 (± 1.0%)</td>
</tr>
</tbody>
</table>

Table 6.6- Efficiency calibration data for ‘Sir Robin’, gamma emission energies and gamma emission data of the radionuclides are taken from the evaluations of the Decay Data Evaluation Project, www.nucleide.org/DDEP.html. The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95%. The uncertainty evaluation has been carried out in accordance with UKAS requirements.
Figure 6.12- Efficiency response of ‘Sir Robin’ where the X-axis is shown on a logarithmic scale at different $\gamma$ ray energies using series of standards of $^{210}\text{Pb}$, $^{109}\text{Cd}$, $^{75}\text{Se}$, $^{57}\text{Co}$, $^{141}\text{Ce}$, $^{75}\text{Se}$, $^{51}\text{Cr}$, $^{137}\text{Cs}$ and $^{54}\text{Mn}$.

6.2.8.2 Alpha-particle spectrometry

The sources were measured on the same set up as the NORM measurements in Chapter 5, the sources prepared by electroplating from a pH adjusted sulphuric acid solution (Hallstadius, 1984) were counted in an ORTEC Octete Plus $\alpha$-particle spectrometer with Passivated Implanted Planar Silicon (PIPS) detectors and ORTEC Maestro, Multichannel Analyser (MCA) application software. The energy calibration of the detectors was performed with a $^{241}\text{Am}$, $^{244}\text{Cm}$ and $^{237}\text{Np}$ source. The sources were counted for 70,000 seconds, in a geometry
with an estimated counting efficiency of 21(5) % based on the solid angle coverage. The instrument backgrounds were measured prior to the sample measurement.

6.2.8.3 ICP-MS

In addition to the separated $^{236}\text{Np}$ and $^{236}\text{Pu}$ samples, mixed stable-element standards were measured using an Agilent 8800 triple quadrupole (ICP-QQQ-MS) to assess the stable element composition. The instrument is equipped with two quadrupole mass filters, separated by an octopole collision-reaction cell. It was fitted with a quartz double-pass spray chamber, MicroMist nebuliser, nickel sample and skimmer cones. The instrument was operated in single quadrupole mode throughout (i.e. with only one mass filter operating), and tuned daily using a mixed 1 $\mu$g·g$^{-1}$ standard solution. Calibration standards were also prepared for $^{236}\text{U}$, $^{237}\text{Np}$, $^{238}\text{U}$, $^{239}\text{Pu}$ and $^{240}\text{Pu}$ to assess instrument sensitivity. The measurement time was approximately five minutes per sample, and the instrument background was counted before and after each sample.

6.2.9 Measurement of isobaric mass distribution of the created fission fragments

The determination of the abundances of each isobaric chain produced by the proton-induced fission of $^{nat}\text{U}$ is complicated by the initial population of a range of elements for each $A$ value in the fission process. The neutron-rich radionuclides produced directly following the fission events typically have radioactive half-lives in the range of seconds to hours. This means that these radionuclides have typically undergone enough radioactive decays to bring their abundances below the minimum detectable activity by the time of the initial $\gamma$-ray spectrometry measurement in the current work. The decay of fission products through their respective mass chains towards stability is generally accompanied by increasing half-lives as the line of stability is approached. Many of the isobaric decay chains from $A \sim 70$ to $\sim 170$ decay through well-defined radionuclide species with some characteristic $\gamma$-ray emissions following their decay by
\( \beta^-\)-emission to excited states in the final, long-lived daughter nucleus of that particular mass chain. These penultimate members of the isobaric fission fragment decay chains can have sufficiently long half-lives (days to months) and are a useful monitor of the decay activity in the present work:

The total number of atoms produced in a given mass chain can be estimated without prior knowledge of the initial elemental \((Z)\) distribution of the members within that mass chain following the initial fission using the assumption that the decay lifetime of the ultimate decay in the chain is significantly longer than each preceding decay half-life.

The basis of any such solution of a decaying nuclear chain must take into account the Bateman equations of radioactive decay (Bateman 1910) for that chain. The number of atoms of the first radionuclide \((N_i)\) within the series is given by the normal exponential decay equation (as described earlier in Chapter 2):

\[
N_i(t) = N_i(0)e^{-\lambda_i t} \quad (Equation \ 6.8)
\]

where \(N_i(t)\) is the number of atoms at time \(t\), \(N_i(0)\) is the initial number of atoms of when \(t = 0\) and \(\lambda_i\) is the decay constant. To model the system, the number of atoms present and their rate of change with respect to time (i.e. the activity) needs to be calculated.

Under the assumption that the parent radionuclide in the chain has a fixed amount of atoms, \(N_i(0)\) at the effective time zero and no further production of the parent radionuclide takes place, then the activity associated with this radionuclide is given by,
\[
\frac{dN_2}{dt} = \frac{d}{dt} N_1(0)e^{-\lambda_1 t} = -\lambda_1 N_1(0)e^{-\lambda_1 t} = -\lambda_1 N_1(t) \quad (Equation \ 6.9)
\]

If \( N_1 \) decays exclusively to a daughter radionuclide \( (N_2) \) then the rate of change of number of atoms of \( N_2 \) is given by;

\[
\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \quad (Equation \ 6.10)
\]

Similar arguments hold for the following nuclei up to and including the terminal radionuclide \( (N_n) \);

\[
\frac{dN_n}{dt} = \lambda_{n-1} N_{n-1} - \lambda_n N_n \quad (Equation \ 6.11)
\]

If the \( n^{th} \) member of the decay chain represents a radioactively stable species (i.e. \( \lambda_n N_n = 0 \)), then;

\[
\frac{dN_n}{dt} = \lambda_{n-1} N_{n-1} \quad (Equation \ 6.12)
\]

A decay simulation was produced based on the matrix based algebraic approach (Appendix E) to the Bateman equations given by Moral, et al, (2003), detector efficiency and \( \gamma \)-ray emission probability so that the effect of varying the initial distribution of radionuclides on the strength of the \( \gamma \)-ray emissions could be measured. It was established that the activity of the longest-lived member in a chain could be related directly to the initial number of atoms at the effective zero time of the irradiation, provided the previous members in the chain were short-lived by comparison. This is indeed the case for most isobaric decay chains between \( A \approx 80-160 \) due to the time it takes for the more neutron-rich, shorter-lived \( (T_{1/2} \approx \text{seconds to minutes}) \) members of a particular mass chain to decay through to the longest-lived member being negligible with
respect to the half-life of the long-lived member, i.e. that closest to stability which can have half-lives of days to months. This approximation overestimates the initial number of atoms by an amount dependent on the initial distribution of the atoms within a particular mass chain. The largest overestimation occurs when the initial atoms in the mass chain are all formed in the chain member with the highest neutron-to-proton ratio (i.e. most neutron-rich). Since the initial elemental distribution was not directly established here, the current work makes the gross assumption of a ‘rectangular distribution’ of the initial elemental population (i.e., an equal elemental production for all isobaric chains of neutron-rich nuclei that there is half-life data for). This was fed into the computational calculation and the overestimation (or underestimation) used to calculate the correction factor to be applied to the measurements. For example, in the case of $^{95}\text{Zr}$ the initial ratio of $^{95}\text{Kr} : ^{95}\text{Rb} : ^{95}\text{Sr} : ^{95}\text{Y} : ^{95}\text{Zr}$ was assumed to be 1:1:1:1:1 and the decay of this system then modelled. This was used to calculate a likely correction factor (between $^{95}\text{Zr}$ measurements and $N_0$). The simulation was then run again with the ratio as 1:0:0:0:0, giving a maximum overestimation. The effective uncertainty in the simulated values arising from the correction factor was estimated to be $\frac{1}{2\sqrt{3}} = 0.29$ multiplied by the maximum overestimation from the true value (this in accordance with a one-standard deviation value for a rectangular distribution). Figure 6.13 shows the results of a simulation for the maximum overestimation of $^{95}\text{Zr}$ as an example. Note that a projection back to $t_0$ based on the number of atoms of $^{95}\text{Zr}$ at the end of the simulation gives good agreement with the actual value of $N_0$ used in the simulation.
Figure 6.13- Results of the simulation used to calculate the maximum overestimation of $N_0$ in the $A = 95$ isobaric chain. The upper plot shows the complex behaviour in the first few seconds after the irradiation as the radionuclides decay towards stability, as well as demonstrating the agreement between projected and actual $N_0$ values. The half-lives of each of the radionuclides in seconds are indicated in the brackets.
6.2.10 Data Analysis of fission fragments

As can be seen in Figure 6.14, the initial fractions showed multiple peaks sitting on a significant background. The background made it challenging to differentiate individual peaks interferences, or instances where a peak was placed on a Compton continuum. Figures 6.15-6.16 show various spectra throughout the 8-month period of the measurements, in order to demonstrate the decay of the fission fragments over the time period.

The data acquisition system used in this work consists of Canberra ADC/MCAs running the Canberra Genie 2000 v2.1C software. The commercial software is used to control data acquisition, determine peak areas and calculate activities using a nuclide library implemented specifically for those samples. The standard live time correction is applied on all detectors. This technique has been demonstrated to work well when the amplifier and ADC are matched and when the observed dead time of the system is no greater than 15%. The first three measurements taken in the analysis had dead-times that were 27.89%, 22.02% and 17.14% respectively, and have thus been omitted from the work.
Figure 6.14- γ-ray spectra of fission fragment ampoule from $^{nat}$U$(p,3n)^{236}$Np irradiation, taken on the 5th February 2014, ~2 months after the target irradiation.
Figure 6.15- Examples $\gamma$-ray spectra of the fission fragment ampoule from the $^{nat}$U$(p,3n)$ $^{236}$Np irradiation for $E_\gamma = 0 – 800$ keV, taken in February, April, July and September 2014, ~2, 4, 7 and 9 months after the target irradiation.
Figure 6.16 - Examples of γ-ray spectra of the fission fragment ampoule from the $^{\text{n}}$U(p,3n)\textsuperscript{236}Np irradiation from $E_\gamma = 800 - 2200$ keV, taken in February, April, July and September 2014, ~2, 4, 7 and 9 months after the target irradiation.
Thus, in order to identify each peak, a procedure utilising three significant steps was established to ensure results with a low degree of uncertainty:

1. An algorithm within the Canberra Genie 2000 v2.1 software was used to perform a background subtraction on the spectra and for peak identification, identifying regions of interest. The interactive peak fitting tool which is based on a Gaussian, was then used to identify any peaks missed, and to ensure that each peak was fitted correctly, and where necessary adjustments were carried out to improve the peak fit. In the event of a second peak being present, where a separate peak was found either side of the Gaussian (found significantly at low energies below 200 keV), the interactive peak fitting was repeated. Once the peak fitting met the user criteria, FWHM where each peak was compared with the previous and following peaks, when the peaks FWHM were found to be within ±0.2 keV, the peak was deemed useable. In instances where the FWHM was either greater or smaller than the identified error, either a further Gaussian was added or the peak was reassessed. The contents of the script were then put into an excel document, with the FWHM, number of counts and peak energies documented.

2. X-rays or γ rays below 30 keV were not taken into account. The emission energies of the peaks of the associated radionuclides were identified (±1 keV) and then searched using the DDEP online database of emission energies. Consequently, the three γ-ray emissions (where possible) with the highest γ-ray intensity were analysed, and identified in the sample spectra. The procedure used meant that the peak had to be clearly displayed in at least three consecutive spectra, to differentiate between genuine peaks and those that were as a consequence of the high background. Once observed, a plot was produced showing the number of counts of a specific peaks region of interest.
versus time. This was then compared to the emission lines of the likely radionuclides, and then used to determine the half-life of a specific radionuclide. This was then listed on the excel database used.

3. The irradiation time used was the effective irradiation time, $t = 0$, using the Zr-Nb chronometry method detailed by Pommé and Collins (2014). By multiplying the counts found in each peak by the $\gamma$-ray emission probability of the specific line and the detector efficiency at the designated energy, an activity calculation was derived of a specific emission peak for each individual radionuclide analysed. Only when all the values for a specific radionuclide were in agreement was the data for the radionuclide used. Where discrepancies were found, these were reviewed and analysed to determine the anomalies found in the measurements.

6.2.11 Experimental results and discussion

6.2.11.1 Fission fragment mass yields for the proton irradiation for the $^{nat}U(p,3n)\ \ ^{236}Np$ reaction

The $\gamma$-ray spectra of the fission products sample were analysed to identify the radionuclides present, with particular emphasis being given to decays identified from neutron-rich radionuclides with mass numbers between $A\sim70$ and $170$ (fission fragments). The corrected activity associated with these specific $\gamma$ ray emissions were plotted as a function of time. The slopes of these individual decay curves were fitted to single-component exponential decay functions to check the radioactive decay half-life was consistent with the evaluated valued for that particular radionuclide. If there was no agreement with published half-lives, other possible sources which could be causing interference were considered and systematically removed until the $\gamma$-emissions were all assigned (as discussed in the previous section). As an example, the 1088 keV line was identified as indicating the presence of $^{123}\text{Sn}$, $^{56}\text{Co}$ or $^{125}\text{Sn}$, however the
half-life was not in agreement with any of their published values. After determining the
activities of $^{56}$Co and $^{125}$Sn from their other $\gamma$-ray emissions, however, their contributions to
the 1088 keV peak could be subtracted, leaving a peak with the correct half-life for $^{123}$Sn.

The activity of the radionuclide at the effective zero time was the calculated independently for
each contributing $\gamma$ emission from each spectrum and the results compared: the effective zero
time was calculated using the $^{95}$Zr-$^{95}$Nb chronometry method detailed by (Pommé and Collins,
2014). If the lines converged to approximately the same activity (when uncertainties in $\gamma$-ray
emission probabilities, detector efficiency and counting statistics were considered) and all of
the above tests were passed then the $\gamma$ emission was considered to have no further unseen
interferences present. The activity at $t_0$ was calculated as the weighted mean of the determined
activities for each $\gamma$ emission for a given radionuclide.

The calculated activity of a radionuclide at the effective time zero ($A_0$) was then converted to
the initial number of atoms ($N_0$) produced for a particular isobaric chain using the simple
relation;

$$N_0 = \frac{A_0}{\lambda} \quad (Equation \ 6.13)$$

where $A_0$ is the effective time zero activity in Bq and $\lambda$ is the decay constant of the final, longest
lived member of the isobaric decay chain. The value was corrected for potential overestimation
utilising the correction factor calculated from the Bateman simulations described in Chapter 2.
The final standard uncertainty was calculated as the quadrature sum of the theoretical uncertainty from the Bateman simulations and the weighted experimental uncertainty calculated in this section (combining spread in the data, counting statistics, full-energy peak efficiency and published emission probability.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>References</th>
<th>Half-lives / days</th>
<th>$\gamma$-emission /keV</th>
<th>$\gamma$-Emission probabilities /%</th>
<th>$N_0$ based on emission/10$^{12}$ atoms</th>
<th>Weighted mean $N_0/10^{12}$ atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{91}$Y</td>
<td>Baglin (2013)</td>
<td>85.51 (6)</td>
<td>1205.0 (7)</td>
<td>0.26 (4)</td>
<td>4.85(75)</td>
<td>4.82(75)</td>
</tr>
<tr>
<td>$^{95}$Zr</td>
<td>Basu et al. (2010).</td>
<td>64.032 (6)</td>
<td>756.729(12)</td>
<td>54.38(22)</td>
<td>6.266(62)</td>
<td>6.246(44)</td>
</tr>
<tr>
<td>$^{103}$Ru</td>
<td>Frenne (2009)</td>
<td>39.255 (8)</td>
<td>497.080(13)</td>
<td>89.5(6)</td>
<td>5.19(18)</td>
<td>5.04(17)</td>
</tr>
<tr>
<td>$^{111}$Ag</td>
<td>Collins et al. (2014)</td>
<td>7.45(1)</td>
<td>342.13(2)</td>
<td>6.68(7)</td>
<td>2.29(62)</td>
<td>2.24(62)</td>
</tr>
<tr>
<td>$^{123}$Sn</td>
<td>Ohya (2004)</td>
<td>129.2(4)</td>
<td>1088.64(10)</td>
<td>0.6(1)</td>
<td>1.14(20)</td>
<td>1.14(20)</td>
</tr>
<tr>
<td>$^{125}$Sn</td>
<td>Katakura (2011)</td>
<td>9.64(3)</td>
<td>1067.10(5)</td>
<td>9.7(26)</td>
<td>*</td>
<td>2.25(53)</td>
</tr>
<tr>
<td>$^{129m}$Te</td>
<td>Timar et al. (2014)</td>
<td>33.6(1)</td>
<td>729.57(5)</td>
<td>0.7(4)</td>
<td>3.8(22)</td>
<td>3.8(22)</td>
</tr>
<tr>
<td>$^{131}$I</td>
<td>Khazov et al. (2006)</td>
<td>8.0233(19)</td>
<td>364.489(5)</td>
<td>81.2(5)</td>
<td>2.19(17)</td>
<td>2.19(17)</td>
</tr>
<tr>
<td>$^{140}$Ba</td>
<td>Nica (2007)</td>
<td>12.753(4)</td>
<td>537.303(6)</td>
<td>24.39(22)</td>
<td>5.577(66)</td>
<td>5.40(26)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>162.6628(24)</td>
<td>6.26(9)</td>
<td>4.84(12)</td>
<td></td>
</tr>
<tr>
<td>$^{141}$Ce</td>
<td>Tuli and Winchell (2001)</td>
<td>32.503(11)</td>
<td>145.443(14)</td>
<td>48.29(19)</td>
<td>4.511(38)</td>
<td>4.511(38)</td>
</tr>
<tr>
<td>$^{144}$Ce</td>
<td>Sonzogni (2001)</td>
<td>284.89(6)</td>
<td>133.544(5)</td>
<td>11.0(2)</td>
<td>4.120(67)</td>
<td>4.14(41)</td>
</tr>
<tr>
<td>$^{147}$Nd</td>
<td>Nica (2009)</td>
<td>10.987(11)</td>
<td>91.105(2)</td>
<td>28.4(18)</td>
<td>1.72(17)</td>
<td>1.81(37)</td>
</tr>
<tr>
<td>$^{150}$Eu</td>
<td>Reich (2012)</td>
<td>15.19(8)</td>
<td>811.77(5)</td>
<td>9.7(8)</td>
<td>0.241(21)</td>
<td>0.243(16)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>88.97(1)</td>
<td>8.4(1)</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1230.71(6)</td>
<td>7.98(66)</td>
<td>0.251(24)</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.7- Table showing the radionuclides that were used in determining the data points used to plot the chart in Figure 6.26.
The $\gamma$-ray emissions and emission probabilities, along with their associated uncertainties, were found from the referenced sources listed. In addition to these nuclei, other radionuclides were identified but not used in the plot as they were either not fission products or could not be used to determine the initial production in that mass chain due to much longer lived, non-gamma emitters earlier in the mass chain. These nuclei included $^{95m}$Nb, $^{106}$Rh, $^{115m}$Cd, $^{124}$Sb, $^{126}$Sb, $^{134}$Cs, $^{136}$Cs, $^{140}$La, $^{56}$Co, $^{125}$Sn, $^{237}$U, $^{88}$Y, $^{88}$Zr, $^{48}$V and $^{46}$Sc. All uncertainties are quoted at $k = 1$. Values marked with an * were identified but contaminated within a single spectrum. $^{56}$Co, $^{48}$V and $^{46}$Sc were formed due to the reaction between the charged particles and the contaminants found in natU or the target material, significantly $^{237}$U is produced as part of the reaction and is not a fission product but rather is likely produced as part of the bombardment of $^{238}$U, a ($p,pn$) reaction as opposed to the ($p,3n$) reaction desired to create the $^{236g}$Np.

Of the radionuclides identified, those corresponding to fission fragments and their daughters’ decays were selected for further analysis. Figures 6.17 to 6.25 show the measured decay curves of $^{95}$Zr, $^{103}$Ru, $^{141}$Ce and $^{144}$Ce. The calculated decay curves were based on a series of $\gamma$-ray spectrometry measurements, where the data points were taken from a series of measurements on ‘Bart’ for a duration of 8 months (from February to September, 2014).
Figure 6.17- Calculated decay curve of $^{95}$Zr, based on a linear scale plot with a fitted $T_{1/2} = 63.71(56)$.

Figure 6.18- Calculated decay curve of $^{95}$Zr, based on a log scale plot, showing an exponential fit.
Figure 6.19- Calculated decay curve of $^{103}$Ru, based on a linear scale plot with a fitted $T_{1/2} = 39.32(89)$.

Figure 6.20- Calculated decay curve of $^{103}$Ru, based on a log scale plot, showing an exponential fit.
Figure 6.21- Calculated decay curve of $^{141}\text{Ce}$, based on a linear scale plot with a fitted $T_{1/2} = 32.63(11)$.

Figure 6.22- Calculated decay curve of $^{141}\text{Ce}$, based on a log scale plot, showing an exponential fit.
Figure 6.23- Calculated decay curve of $^{144}$Ce, based on a linear scale plot with a fitted $T_{1/2} = 282(13)$.

Figure 6.24- Calculated decay curve of $^{144}$Ce, based on a log scale plot, showing an exponential fit.
Specifically, only those nuclides which were not preceded in their decay chains by longer-lived nuclides were considered. These were converted to a fission yield (expressed as a percentage) and scaled so that the $^{95}$Zr yield was in agreement with the published value for 14 MeV neutron
bombardment (Kellett, et al, 2009) when the total published yields are standardised to add to 200% (as each fission event would result in two residual nuclei). This point was chosen for standardising as the $^{95}$Zr value had the lowest uncertainty. Figure 6.26 shows these data points from the current work along with the JEFF 3.1.1 (Kellett, et al, 2009) database values for the fission mass distribution expected from 14 MeV neutrons on $^{238}$U as a comparison.

The experimental data points on the two mass abundance peak regions at $A \approx 95$ and $A \approx 140$ are in good agreement with the published values based on 14 MeV neutron irradiations (Kellett, et al, 2009). There are however some noticeable differences with the trough between the two peaks corresponding to near-symmetric fission (i.e. the data for mass chains between $A \approx 110$ and 130) being less prominent for the proton-induced data from the current work, indicating higher yields of these nuclides in this bombardment. In addition, the data for $^{156}$Eu also indicates a higher yield of this mass chain was found in the JEFF 3.1.1 evaluation.

It has been found in the nuclear database JEFF 3.1.1 that, for neutron induced fission, the shape of the yield distribution changes in a predictable way as the energy of the incident neutrons is varied. Specifically, the relative fission yields for near-symmetric fission (mass chains 110-130) increase and the gradient of the fission yield curve adjacent to this mass region decreases as the neutron energy increases. This corresponds to an increase in the fission yields of mass chains that are not on the peaks. As the energy of the protons is almost double that of the closest available neutron irradiation data, it is likely that the differences are due to this increased energy rather than a major difference between proton and neutron irradiations. This is further supported by the good agreement between the experimental and published data for the points located around the peaks, which do not change with energy. The lower than predicted yield observed for the $A = 131$ chain (which was evaluated using decay of $^{131}$I) may arise due to the
volatile chemical nature of iodine and the possible related loss of material during the chemical processing of the target.

Figure 6.26- A plot of yield per fission event (%) vs mass number (A) of the mass chains for the induced fission of natural uranium. The data points represent the values found during this experiment (irradiation with 25 MeV protons) whilst the dashed line represents the data for 14 MeV neutrons as derived from JEFF 3.1.1. The uncertainties on this data represent an uncertainty of one standard uncertainty. Error bars are at \( k = 1 \). Note \(^{95}\text{Zr}\) is marked in red, as it was used for normalisation of the plot.

Thus overall the results obtained from this study of fission products derived from the proton irradiation of natural uranium has shown that the yield distribution plot obtained is in good
agreement with the referenced value obtained from the neutron induced fission with 14 MeV neutrons as published in JEFF 3.1.1. The shape of the yield distribution displays variations consistent with the trend of increasing energy seen as incident neutron energy is varied.

6.2.11.2 Identification of $^{236}$Np via γ-ray and α-particle spectrometry produced by proton irradiation of natural uranium target ($^{\text{nat}}\text{U}(p,3n)^{236}\text{Np}$)

6.2.11.2.1 Methodology for determination of the $^{236}\text{Np}$ content

The decay of the long-lived, high-spin coupling ground state in $^{236}\text{Np}$ ($^{236}\text{gNp}$) proceeds by both β⁻ decay to $^{236}\text{Pu}$ and by electron capture to $^{236}\text{U}$ (Browne and Tuli, 2006) with branching ratios of approximately 13% and 86.3% respectively. The metastable excited state in $^{236}\text{Np}$ ($^{236}\text{mNp}$) decays by β⁻ and electron capture to $^{236}\text{Pu}$ and $^{236}\text{U}$ respectively. The branching ratios for these competing decay branches from $^{236}\text{mNp}$ are listed as 50(3) % for each decay mode in the most recent nuclear data evaluation (Browne and Tuli, 2006).

To guide this analysis, Figure 6.27 shows calculated grown-in and decay curves using the standard laws of radioactive decay for the decays associated with the decay and feeding from the $T_{1/2} = 1.55 \times 10^5$ year $^{236}\text{Np}$ ground state and $T_{1/2} = 22.5(4)$ hour metastable state.
Figure 6.27- Calculated decay and grow-in curves for $^{236}$Np, $^{236}$Pu and $^{236}$U. These assume a production of $10^{15}$ initial $^{236}$Np atoms at a notional time $t = 0$ in both the ground ($T_{1/2} = 1.55 \times 10^5$ years) and metastable ($T_{1/2} = 22.5$ hours) states. Note that three years after the irradiation time, the main activity arises from the $\alpha$ decay of $^{236}$Pu ($T_{1/2} = 2.858$ years) which is formed following the decay of the $^{236}$Np metastable state and has a much shorter decay half-life than the parallel $^{236}$U decay branch ($T_{1/2} = 2 \times 10^7$ years). Although the number of atoms produced are similar, the activity of $^{236}$U is six orders of magnitude less than $^{236}$Pu due to its much longer decay half-life of $2.3 \times 10^7$ years. The number of $^{236}$Pu atoms created following the decay of the $^{236}$Np ground state is more than six orders of magnitude less than the number created following the decay of the isomeric state.

6.2.11.2 Using $\gamma$ rays from the 86% electron capture branch

The most direct signature of $^{236g}$Np is the detection of $\gamma$ rays from the $6^+ \rightarrow 4^+ \rightarrow 2^+ \rightarrow 0^+$ cascade in $^{236}$U, populated by the electron-capture branch of the $^{236g}$Np decay ($\epsilon = 86.3\%$). This cascade results in the emission of the $\gamma$ rays of energy 160, 104, and 45 keV, (Table 6.1), (Browne and Tuli, 2006). In this experiment, detection of these discrete energy signature $\gamma$ rays is
complicated by the $\gamma$ ray background produced by the large quantity of fission products generated by $^{235,238}\text{U}(p,f)$ reactions. Although the $I^=6^+$ excited state in $^{236}\text{U}$ state is the main directly populated state in the electron capture of $^{236}\text{Np}$, the subsequent transitions in the $\gamma$-ray decay cascade are all rather highly converted with total internal conversion coefficients of $\alpha_{tot} = 1.8, 11$ and 604 for the 160.3, 104.2 and 45 keV stretched E2 $\gamma$ ray transitions in $^{236}\text{U}$ respectively (Kibédi, 2008).

The $\gamma$ ray spectrum measured on ‘Lancelot’ displayed in Figure 6.28 shows transitions associated with decays from fission-product decay daughters with half-lives of the order of a year or more year such as $^{137}\text{Cs}$, $^{106}\text{Ru}-^{106}\text{Rh}-^{106}\text{Pd}$; $^{125}\text{Sb}-^{125}\text{Te}$; and $^{144}\text{Ce}-^{144}\text{Pr}$. The comparable $\gamma$-ray spectrum for the separated neptunium fraction shows the majority of these can be removed/reduced in this spectrum compared to the target material fraction.
Figure 6.28- Gamma-ray spectra measured for 250,000 seconds to show the effects of the chemical separation scheme on the target material. The measurement was taken 2 years and 9 months after the initial target irradiation.
Figure 6.29 shows the γ-ray spectrum from the separated Np fraction as measured in a HPGe well detector ‘Sir Robin’ which had an increased sensitivity for low-energy gamma rays and higher overall full-energy peak detection efficiency compared to ‘Lancelot’. In addition to the fission fragments, lines are also evident in the target fraction spectrum which are associated with the decay daughters of members of the Thorium (4n) natural decay series.

![Gamma-ray spectrum](image)

Figure 6.29- Gamma-ray spectrum of 1 g of the initial target fraction following the neptunium separation, as measured in the well HPGe detector. The live time for this spectrum was $2.16 \times 10^5$ s. The measurement was taken 2 years and 9 months after the initial target irradiation.
These are created in the target following the α decay of $^{236}\text{Pu}$ to $^{232}\text{U}$ and its subsequent decay to $^{228}\text{Th}$ which decays down the traditional Thorium 4n series terminating at $^{208}\text{Pb}$. Notably, some of these α decay lines from the Thorium 4n series are also identified in the α-particle spectrometry part of this work (Figure 6.30).

Figure 6.30- Alpha-spectra to show the effects of the various stages of the chemical separation scheme on the target material.
The main difference between the Np fraction to the unseparated target fraction is the relative increase in the intensity of the K-shell X-ray close to 90 keV. These could arise from the Np electron capture branch, but are also possibly emissions following internal conversion from excited states populated in the U, and Pu daughters.

6.2.11.2.3 Estimated $^{236}$Np production based on $\gamma$-ray spectrometry measurement

A 1 g ampoule was taken for $\gamma$-ray spectrometric measurements (from an overall total target material mass of 40.21). It must be noted that no tracer was used in this work to monitor yield (in order not to contaminate the sample); $^{239}$Np had previously been investigated as a yield tracer but this may produce a peak in the germanium detector spectrum at 160.985 keV due to summation between the Pu K$_{\alpha 2}$ X-ray and a coincident 61.46 keV $\gamma$-ray emission depopulating the 392 keV level of $^{239}$Pu.

Using the expected intensity of the 160.3 keV $\gamma$ ray transition (the $6^+ \rightarrow 4^+$ transition in $^{236}$U), an MDA activity of <3 Bq was estimated in these measurements for $^{236}$Np, however, an accurate quantitative estimate was not possible in the current work since the identification of the $\gamma$ ray peak itself was not clear (result at the MDA) in spectra shown in Figures 6.28 and 6.29. Figure 6.29 shows the limits for the measurement of the 160 keV transition measured in the well detector. The transition at this energy is at the limit of detection, but a background subtracted fit to the peak region yields approximately $1.4(4) \times 10^5$ counts in a $2.16 \times 10^5$ s counting period. Estimating a full-energy peak efficiency of 50 (20) % for the well detector system at 160 keV, corresponds to an activity in the total dissolved target mass material (including nitric acid, approximately 40 grams) of 52 (26) Bq for the 160 keV branch. With corrections for internal conversion ($\alpha(E2:160 \text{ keV}) = 1.8$) and the assumed electron capture/$\beta^-$ branching ratio in the decay of $^{236}$Np (86% electron capture branch to $^{236}$U), this spectrum then
gives an estimate of the $^{236}$Np total target activity of approximately, $170 \, (85) \, \text{Bq}$, which corresponds to $1.2(6) \times 10^{15}$ produced atoms. This is in line with the estimated production described in section 6.3.3 of the current work.

6.2.11.2.4 Time dependence of the $^{236}$Pu activity and extrapolated $^{236}$Pu production at production time zero

In the current analysis, the clean signature of the $\alpha$ decay of $^{236}$Pu (Figure 6.30) ($T_{1/2} = 2.858(8)$ years (Browne and Tuli, 2006)) could be detected (Table 6.8). From the chemical separations conducted to isolate Pu, the signature energy peaks from the $\alpha$ decay of $^{236}$Pu are $5720.87 \, (10)$ keV and $5767.53 \, (8)$ keV with an intensity of $30.8 \% \, (3)$ and $69.1 \% \, (3)$ respectively (Browne and Tuli, 2006). There is no mechanism to make $^{236}$Pu ($Z = 94$) directly in the reaction $\text{U}(p,xn)$ and therefore the presence of Pu in the sample is attributed to stem from the $\beta^-$ decay of $^{236}$Np or $^{236m}$Np. Due to the isomeric state half-life of $22.5 \, (4)$ hours, all $^{236m}$Np would have decayed within the target prior to the chemical separation procedure, accounting for the vast majority of the $^{236}$Pu in the sample. As Figure 6.27 shows this is by far the largest contribution to the total amount of $^{236}$Pu even assuming a reduced isomeric isomer ratio due to the factor $6 \times 10^7$ difference in the half-lives of the metastable state and ground state in $^{236}$Np.
Table 6.8 – Alpha decay energies of radionuclides of interest $^{238}$U, $^{236}$U, $^{235}$U, $^{234}$U, $^{232}$U, $^{232}$Th and $^{236}$Pu.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life</th>
<th>Characteristic $\alpha$-decay energies (keV)</th>
<th>$\alpha$-decay intensity (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}$U</td>
<td>$4.468 \times 10^9$ y</td>
<td>4151 (5) 4198 (3)</td>
<td>21 % (3) 79 % (3)</td>
<td>Browne and Tuli, 2007</td>
</tr>
<tr>
<td>$^{236}$U</td>
<td>$2.343 \times 10^7$ y</td>
<td>4445 (5) 4494 (3)</td>
<td>26 % (4) 74 % (4)</td>
<td>Browne and Tuli, 2006</td>
</tr>
<tr>
<td>$^{235}$U</td>
<td>$7.038 \times 10^8$ y</td>
<td>4364 (4) 4395 (4) 4415 (5) 4556 (4) 4597 (4)</td>
<td>19 % (14) 58 % (24) 3 % (6) 4 % (6) 5 % (7)</td>
<td>Browne and Tuli, 2012</td>
</tr>
<tr>
<td>$^{234}$U</td>
<td>$2.455 \times 10^5$ y</td>
<td>4722 (14) 4775 (14)</td>
<td>28 % (9) 71 % (16)</td>
<td>Browne and Tuli, 2012</td>
</tr>
<tr>
<td>$^{232}$U</td>
<td>$68.9$ y</td>
<td>5263 (9) 5320 (14)</td>
<td>32 % (23) 68 % (23)</td>
<td>Abusaleem, 2014</td>
</tr>
<tr>
<td>$^{232}$Th</td>
<td>$1.405 \times 10^{10}$ y</td>
<td>3947 (20) 4012 (14)</td>
<td>22 % (13) 78 % (13)</td>
<td>Abusaleem, 2014</td>
</tr>
<tr>
<td>$^{236}$Pu</td>
<td>$2.858$ y</td>
<td>5721 (10) 5768 (8)</td>
<td>31 % (3) 69 % (3)</td>
<td>Browne and Tuli, 2006</td>
</tr>
</tbody>
</table>

6.2.11.2.5 Estimated $^{236}$Pu production at effective time zero based on $\alpha$-spectrometry

An analysis was carried out using $\approx \frac{1}{40}$ of the total dissolved target material, with a sub-fraction of the target material taken for $\alpha$-spectrometry being 0.020 (4) g. The $\alpha$ measurements were performed prior to any chemical separation and therefore no correction is required for separation recovery.

In order to determine the $^{236}$Pu activity, $A_0$, from the original target material at effective time zero, the measured $^{236}$Pu was used to show total activity three years after the irradiation and the decay half-life of $T_{1/2} = 2.858(8)$ years $= 9.0 \times 10^7$ seconds. Estimating the geometrical counting efficiency of $\alpha$-particle spectrometry to be 21(5) % and using the counts measured associated with the $^{236}$Pu $\alpha$-emissions at 5720.87 (10) keV and 5767.53 (8) keV (relative
intensities of 30.8 % (3) and 69.1 % respectively) (Table 6.8) 5.66 × 10^5 counts was measured in the Pu region of interest over a counting time of 70,000 seconds. This corresponds to a lower limit estimate of the total target activity associated with 236Pu of 8 (3) × 10^4 Bq at the time of measurement and 1.5 (5) × 10^5 Bq at the time of production.

Taking into account the half-life of 2.858(8) years for 236Pu leads to a lower-limit estimate for the total number of 236Pu atoms produced following decay of 236mNp of 2.0(7) × 10^{13}. Assuming a 50% branching ratio for the decay of this isomer 4.0(1.4) × 10^{13} atoms created in the metastable state. Note that this should be considered as a lower limit, which does not include counting losses for example for uptake of the Pu onto the counting discs. This is consistent with the preferential feeding of the high-spin ground state in 236Np following the (p,3n) fusion evaporation reaction.

6.2.11.2.6 Detecting 236U activity

236U is produced by the electron capture decay of 236gNp and 236mNp. It subsequently α decays to form 232Th. As in the previous case, the time dependence of the 236U activity can also provide a measurement of the 236gNp present in the sample. The relatively long half-life of 236U (T_{1/2} = 2.3 ×10^7 years) means that the amount of 236U produced by 236gNp increases continually over the counting period, while the amount due to the isomer decay reaches a saturation value within the order of a week after the irradiation period. The half-life for 236U means a reduced activity compared to the much shorter lived 236Pu branch. The fact that the half-life of 236U is six orders of magnitude longer than the competing 236Pu decay branch means that very little activity is observed via the α-decay measurements in the current work. A potential complication in the sample measurement is the presence of 235U from the natural uranium target material whose main α decays peaks at 4364 (4) and 4395 (4) keV (Browne and Tuli, 2013) partially overlap
to the $\alpha$ peak in the decay spectrum of $^{236}$U (Figure 6.30) which are at: 4445 (5) and 4494 (3) keV (Browne and Tuli, 2006).

6.2.11.2.7 ICP-MS measurement of simulated fission products and separated target

A 100 $\mu$g/g simulated fission product solution was loaded onto a 2 g pre-packed TEVA resin cartridge in 10 mL 2.5 M HNO$_3$ with ascorbic acid in the presence of Fe$^{3+}$, followed by an additional 10 mL wash with the same solution. This was followed by 10 mL 9 M HCl + 0.1 M of NH$_4$I, and 10 mL of 0.1 M HCl, representing the $^{236}$Pu and $^{236}$Np elution fractions, respectively. A 1 mL aliquot of each fraction was diluted to a total volume of 10 mL with 2% HNO$_3$ for ICP-MS measurement with the recovery assessed by comparing the counts in each fraction to the counts in the load solution. No fission products were detected in the Pu and Np elution fractions, with the detection limit equivalent to a recovery of 0.1%. The recoveries in the load and wash fractions ranged from 44% (Nb) to 66% (La), suggesting that there is some retention on the resin, this may be improved by an increased wash volume.

An important consideration for the target sample is the very high activities of fission products (> 50 MBq, depending on cooling time), which affects the performance of the resin column. In the $^{236}$Pu and $^{236}$Np eluted fractions, the U activity was reduced by 3 orders of magnitude compared to the load solution as a result of the 2.5 M HNO$_3$ + ascorbic acid + Fe$^{3+}$ wash, however the U content was still very high, and further separation is required.

The mass resolution of ICP-MS cannot differentiate between $^{236}$U, $^{236}$Pu and $^{236}$Np. However, elevated counts were measured at mass 236 using $\sim \frac{1}{40}$ of the total dissolved target material before taking a $^{236}$Np elution fraction, and $^{237}$Np was also detected, suggesting that $^{236}$Np is
present. Additionally, given the high U content, there may be some contribution from $^{236}$U, which, based on this timescale, would be formed following the decay of $^{236m}$Np, which would give rise to a similar amount of $^{236}$Pu atoms based on its branching ratios. Assuming all counts at mass 236 were from the Np ground state, the activity concentration in the undiluted sample was $2.2 \pm 0.1$ Bq/g (uncertainty from the counting statistics only). The results highlight the importance of a more extensive clean-up of the separated neptunium in order to get conclusive results.

6.2.12 Summary of results from the production of $^{236}$Np

The final certified values are all derived by the $\gamma$-ray and $\alpha$-spectrometry results:

Date of Calibration- 11 December 2013
Sample type- A 1 g ISO ampoule from an overall total target material mass of 40.21.

Based on 160.3 keV $\gamma$ ray transition (the $6^+ \rightarrow 4^+$ transition in $^{236}$U), an MDA activity of <3 Bq ± 100%*

*Identification of the $\gamma$ ray peak itself was not clear as shown in spectrata Figures 6.28 and 6.29.

Based on $\alpha$-emissions at 5720.87 (10) keV and 5767.53 (8) keV an activity of $1.5(5) \times 10^5$ Bq at the reference date provided.
Chapter 7

7. Summary and Future Work

7.1 Summary of current progress and commercial applications of work

7.1.1 NORM reference materials

The European Metrology Research Programme (EMRP) project IND57 (MetroNORM) seeks to address some of the measurement challenges by investigating present state-of-the-art and suggesting improvements and novel developments for:

• reference materials and sources
• in situ measurement systems and sampling methods
• standardisation and development of measurement procedures
• improvements of NORM related nuclear decay data

This work has been concerned with MetroNORM work package one (reference materials and sources) and the measurements carried out at NPL to certify these materials as reference standards. Having standardised the reference materials, to further validate the findings in this work, the materials were sent to the respective laboratories involved in the project for them to perform $\gamma$-ray spectrometry on the NPL certified reference materials as part of a NMI intercomparison. In addition, TiO$_2$ and Tuff were used to calibrate LaBr$_3$ detectors that were used for the in-situ measurement systems methods part of the project. Finally, the techniques utilised in the EngD thesis in regards to the production of these materials have been used to develop measurement solutions and an E-Learning course, to ensure the correct characterisation of real reference materials with complex procedures, with many of the methods utilised being applicable for use, not only in the nuclear industry but also in the growing fracking sector. The
materials have already been sent to some commercial NORM assay laboratories, to help calibrate their instrumentation, and similar materials will be used in future NPL Proficiency Test Exercises.

7.1.2 Production of $^{236}$Np

A radiochemical scheme has been developed for the separation of Np and Pu from fission fragments, produced as part of the target irradiation of natural uranium. The spectrometric analysis shows that the chemical separation scheme adopted separates Pu from fission fragments and other $\alpha$ emitting radionuclides, including the target uranium material. The results used to identify the production of Np are more complicated. The $\gamma$-ray spectroscopy used shows the signature $\gamma$ ray for the decay of the $^{236}$Np ground state 160.3 keV at the minimum detectable activity in the current work. The presence of $^{236}$Pu characteristic lines in the $\alpha$-spectrometry analysis indicates the production of its $^{236}$Np mother nucleus in the metastable state at a level of at least $4 \times 10^{13}$ atoms. The ICP-MS measurement show an elevation at mass 236, however it was not possible to differentiate between the isobaric triplet $^{236}$U, $^{236}$Pu and $^{236}$Np in the current work. Making it very difficult to certificate and validate the activity of the $^{236}$Np and thus sell as a certified reference standard. To be able to characterise it accordingly, further chemical clean-up of the material will be needed.

However, the work has shown an ability to produce a clean source of $^{236}$Pu which is of interest as a chemical yield tracer for the radiochemical analysis of $^{238}$Pu, $^{239}$Pu, $^{240}$Pu and $^{241}$Pu from nuclear fuel. Radiochemical analysis of plutonium in nuclear fuel is complicated by the few radionuclides suitable for tracing: $^{236}$Pu, $^{242}$Pu and $^{244}$Pu. A limited supply of $^{242}$Pu and $^{244}$Pu (Jerome, et al, 2012) are available, making $^{236}$Pu, as the most convenient radotracer. Currently, a widely used production mechanism for $^{236}$Pu is through the photon irradiation of
237Np \( (\gamma, n) \) 236Pu (Efurd, 1990). However, this work has shown that the charged-particle irradiation of natural uranium (\( \text{nat} U (p,3n) 236\text{Np} \)) can also provide a mechanism to produce 236Pu. This production has led to NPL finding a new production route for 236Pu and led to cost savings of \( \sim 45\% \) in comparison to its current supplier of 236Pu.

7.2 Future work

7.2.1 NORM reference materials

Further work will look at reducing uncertainties of the reference materials especially for the measurements of 210Pb and 210Po. In addition, there needs to be a much better agreement between the radiometric measurements and mass measurements carried out, further validation work is already underway to address this. A greater number of samples must be measured, for the radiochemical analysis to account for improved heterogeneity in the samples. Finally, the methods and procedures developed will be applied to a wider range of industries, such as mining but also with the growing UK fracking sector.

7.2.2 Production of 236Np

The Nuclear Forensics, Safeguards, Proliferation Detection, Treaty Monitoring, Bioassay and Consequence Management program sample analysis communities currently have identified the measurement of neptunium isotopes as a priority need, especially a mass spectrometry compatible isotope dilution tracer for 237Np measurement. There is only one suitable radionuclide that can fulfil this role: 236gNp.

Future work may be to carry out investigating and systematising existing production cross section data such as for 236U target (Appendix G), supplementing this with theoretical calculation of production cross sections. In addition, the chemical processing of irradiated
targets needs to be further optimised, and the outcomes of these two activities will lay the foundations for test irradiations aimed at maximising production of this nuclide in a suitably pure state for use as an isotope dilution mass spectrometry tracer. The work carried out in this EngD thesis at NPL has identified a radiochemical separation of neptunium from irradiated uranium. This is based on solvent extraction and extraction chromatography. Although this approach has been generally successful, it remains to be optimised in several ways: the separation of neptunium (ng-µg quantities) from the bulk (1-2 g) uranium target is dependent on solvent extraction, isolation of neptunium is straightforward with extraction chromatography techniques. However, this needs to be further developed to ensure all residual fission products are removed without adversely impacting the neptunium recovery. Finally, a certified $^{236}$Np standard certificate will need to include the detailed optimum irradiation conditions for the production of $^{236}$Np, the chemical processing necessary to recover the $^{236}$Np produced, and the measurement and calibration of the final product in such a way that these steps can be replicated by other laboratories with access to similar facilities.
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Appendix A

Alpha-spectrometry linearity and procedure development

This procedure identifies the proper operation and use of low level environmental alpha spectrometry to carry out the quantitative determination of the activity of individual radionuclides. The document has been produced in order to give the customer, the auditor and the radiochemistry team at NPL confidence in the test reports produced.

Linearity/accuracy test

<table>
<thead>
<tr>
<th>Purpose</th>
<th>To confirm the range over which the test is linear.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pass/fail criteria</td>
<td>To identify at which point the source loses spectral quality and thus peak energy ratios cannot be determined and the spectral resolution fails.</td>
</tr>
<tr>
<td>Method used</td>
<td>Using a solution of $^{232}$U (NPL tracer) and Unat (analyte) (ratio 1: 20.5) a series of electrodeposited disks were made to test the linearity of the assay of $^{238}$U. The $^{238}$U value is traceable to NPL standards. Using the solution the following sources were produced in order to determine/confirm the $^{238}$U value of the original certificated Unat solution:</td>
</tr>
<tr>
<td></td>
<td>• Dispense 1 drop of active solution into a bottle and prepared for electrodeposition. (~24 Bq).</td>
</tr>
<tr>
<td></td>
<td>• Dispense 2 drop of active solution into a bottle and prepared for electrodeposition. (~48 Bq).</td>
</tr>
<tr>
<td></td>
<td>• Dispense 4 drop of active solution into a bottle and prepared for electrodeposition. (~96 Bq).</td>
</tr>
<tr>
<td></td>
<td>• Dispense 0.2 drop of active solution into a bottle and prepared for electrodeposition. (244 Bq).</td>
</tr>
<tr>
<td></td>
<td>• Dispense 0.5 drop of active solution into a bottle and prepared for electrodeposition.</td>
</tr>
<tr>
<td></td>
<td>• Dispense c.1g of active solution into a bottle and prepared for electrodeposition.</td>
</tr>
<tr>
<td>Date measurements carried out</td>
<td>16/10/2012 to 22/10/2012</td>
</tr>
<tr>
<td>Materials used</td>
<td>NPL standards and Six electrodeposited discs at varying concentrations.</td>
</tr>
</tbody>
</table>
Results

<table>
<thead>
<tr>
<th>Activity of alpha spec Source</th>
<th>Measured U-238 Value (Bq/g)</th>
<th>Uncertainty (Bq/g)</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>~24 Bq</td>
<td>1153</td>
<td>83.18</td>
<td>18.00</td>
</tr>
<tr>
<td>~48 Bq</td>
<td>1134</td>
<td>60.96</td>
<td>27.00</td>
</tr>
<tr>
<td>~96 Bq</td>
<td>1108</td>
<td>59.01</td>
<td>44.00</td>
</tr>
<tr>
<td>~244 Bq</td>
<td>1192</td>
<td>64.83</td>
<td>56.00</td>
</tr>
<tr>
<td>~610 Bq</td>
<td>1176</td>
<td>52.75</td>
<td>64.00</td>
</tr>
<tr>
<td>~1.2 kBq</td>
<td>Could not be measured due to poor spectral resolution.</td>
<td>-</td>
<td>98.00</td>
</tr>
<tr>
<td>Mean Value (Bq/g)</td>
<td>1,152.6</td>
<td>64.146</td>
<td></td>
</tr>
</tbody>
</table>

Criteria

To measure $^{238}$U activity concentration to ensure the sources are not significantly different from each other. Up to 1kBq total activity (due to combined peaks of $^{238}$U and $^{234}$U) are linear anything over that produces poor peak resolution and thus no clear energy separation.

Pass/fail

Passed. All sources up to 1kBq.

Range test

<table>
<thead>
<tr>
<th>Purpose</th>
<th>To confirm that the method meets the customer’s specification.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pass/fail criteria</td>
<td>At which point does the dead time yield high uncertainties and at which point in the accuracy test does the spectral resolution prove to be insufficient.</td>
</tr>
<tr>
<td>Method used</td>
<td>Assessment from the results from the linearity, accuracy and precision tests but also by looking at the measurement of $^{211}$Pb and its decay to understand up to what dead time the detector can produce satisfactory spectra with a low uncertainty.</td>
</tr>
<tr>
<td>Date assessment carried out</td>
<td>16/10/2012 to the 18/10/2012</td>
</tr>
<tr>
<td>Results</td>
<td>From the Unat measurements it is evident all measurements up to a 1kBq yield sufficient shaped peaks and with decent peak resolution (FWHM). As well as this the detector functions yielding results with a low uncertainty up to 10% dead time. Anything over this the standard deviation and uncertainty of measurement prove to be problematic.</td>
</tr>
<tr>
<td>Criteria</td>
<td>Any measurement producing a 10% dead time or greater than 1kBq in activity is deemed to be above the range limit.</td>
</tr>
<tr>
<td>Pass/fail</td>
<td>Passed</td>
</tr>
</tbody>
</table>
Scatter graph of dead time vs decay corrected count time/live

The low R2 of 0.157 value shows that the data fits a straight line well; additionally, the gradient function is low showing a constant fit.
Appendix B

**SWORD model for γ-ray spectrometry and activity concentration determination**

The SWORD model was based largely on manufacturer provided detector dimensions supplemented by previous experience in modelling the same detector incorporating some estimations, for example in the radius of the corners, the size and shape of the internal hole and the depth and composition of the dead layers. The model was unchanged between runs other than the composition of the source. The modelled efficiency was determined by dividing the output spectrum, to which no artificial broadening had been applied, into 8k channels and calculating the “peak” area as:

\[
N = n_{i-1} + n_i - \frac{1}{2} (n_{i-3} + n_{i-2} + n_{i+1} + n_{i+2})
\]

The model was validated by measurements with a set of three mixed radionuclide standards in 4 mol dm\(^{-3}\) hydrochloric acid traceable to national standards [NPL R08-03, ref]. Across the energy range 60 keV to 1836 keV the difference between modelled and measured photopeak efficiency was typically 2 % although increased to 5 % at lower energies. The ratio between the photopeak detection efficiency for the matrix concerned and that for distilled water as a function of energy was parameterised using a nonlinear least squares fit using a Gauss-Newton algorithm written for Matlab. In some cases, (for example dilute acids) the correction approaches unity as the energy increases above 500 keV therefore a skewed error function was used. In other cases, the correction does not approach unity until much higher energies so the skewed error function was convoluted with a function of the form \(y(x) = 1 - 1/x\) to allow a more gradual approach to unity.

In the case of 0.5 mol dm\(^{-3}\) nitric acid, the difference in attenuation between “pure” water and acid was less than the statistical uncertainty of the simulations, so no correction was applied. In the case of 4 mol dm\(^{-3}\) hydrochloric acid, there was a small but significant difference. The ratio of modelled efficiency in the acid to the water was modelled with the function:

\[
f(X; a) = 2 \text{erf}(a_1X + a_2) - 1
\]

Where

\[
X = \frac{E}{E_{\text{min}}}; E_{\text{min}} = 50 \text{ keV}
\]

The value of \(E_{\text{min}}\) was pre-selected as being slightly lower than the minimum energy of interest. The first derivatives of the function with respect to each fitted parameter are required by the fitting algorithm used and these are:

\[
\frac{df}{da_1} = \frac{4X}{\sqrt{\pi}} \exp(-(a_1X + b)^2)
\]

\[
\frac{df}{da_2} = \frac{4}{\sqrt{\pi}} \exp(-(a_1X + b)^2)
\]

Therefore each row \(i\) of the residual vector is given by:
\[ r_i = f_i - 2 \text{erf}(a_1 X_i + a_2) + 1 \]

Each row of the Jacobian matrix is given by:

\[
J_i = \begin{bmatrix}
-\frac{4X_i}{\sqrt{\pi}} \exp(-(a_1 X_i + b)^2) & -\frac{4}{\sqrt{\pi}} \exp(-(a_1 X_i + b)^2)
\end{bmatrix}
\]

However, in the case of the solid matrices the self-attenuation is significantly greater than for water across the whole energy range considered, and an adjustment was required to allow the upper part of the model curve to have a finite gradient while still asymptotically approaching unity. The fitting function used was therefore modified to:

\[
f(X; a) = 2 \left(1 - \frac{a_3}{X}\right) \text{erf}(a_1 + a_2 X) - 1
\]

In this case each row of the Jacobian matrix of derivatives is given by:

\[
J_i = \begin{bmatrix}
-\frac{4}{u(f_i) \sqrt{\pi}} \left(1 - \frac{a_3}{X_i}\right) \exp(-z^2) & -\frac{4X}{u(f_i) \sqrt{\pi}} \left(1 - \frac{a_3}{X_i}\right) \exp(-z^2) & \frac{2 \text{erf}(z)}{X_i u(f_i)}
\end{bmatrix}
\]

Results for 4 mol dm\(^{-3}\) HCl vs. water

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_1)</td>
<td>0.06213762</td>
</tr>
<tr>
<td>(a_2)</td>
<td>1.754236</td>
</tr>
<tr>
<td>(E_{\text{min}})</td>
<td>50 keV</td>
</tr>
</tbody>
</table>

Results for solid matrices vs. water

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_1)</td>
<td>1.156355</td>
</tr>
<tr>
<td>(a_2)</td>
<td>0.7481218</td>
</tr>
<tr>
<td>(a_3)</td>
<td>0.04321840</td>
</tr>
<tr>
<td>(E_{\text{min}})</td>
<td>40 keV</td>
</tr>
</tbody>
</table>
Figure B2.1 shows the correction factor (ratio of the full energy peak efficiency in matrix to that of water) as a function of energy for 4 mol dm$^{-3}$ hydrochloric acid. Note the data itself does not merit the use of a function more complex than a straight line, however the skewed error function was selected to reflect the underlying physics and based on experience with other matrices.
Figures B2.2, 2.3 and 2.4 show the correction factor (ratio of the full energy peak efficiency in matrix to that of water) as a function of energy for Sand, Titanium Dioxide (TiO$_2$) and Tuff respectively. Red points represent the Monte Carlo data and the green line represents the fitted model. Uncertainty bars shown represent twice the statistical (type A) uncertainty.

Sand:
Titanium dioxide.
Appendix C

Activity concentration determination

Specific activity concentration in a given reference material sample is given by:

\[ A = \frac{C_{\text{net}}}{E_f P_\gamma t s mK} \]

Where \( C_{\text{net}} \) is the corrected net peak area in the sample spectrum, \( E_f \) is the efficiency of the full energy peak, \( P_\gamma \) is the \( \gamma \) emission probability, \( t_s \) is the live time in seconds, \( m \) is the mass of material in kg and \( K \) is the various correction factors \((K = K_1 \cdot K_2 \cdot K_3 \cdot K_4 \cdot K_5)\).

\( K_1 \) is the correction factor for nuclear decay:

\[ K_1 = \exp \left[ -\frac{\ln 2 \cdot \Delta t}{T_{\frac{1}{2}}} \right] \]

\( \Delta t \) is the elapsed time between sample collection and measurement while \( T_{\frac{1}{2}} \) is the radionuclide half-life.

\( K_2 \) is the correction factor for the nuclide decay during counting period:

\[ K_2 = \frac{T_{\frac{1}{2}}}{\ln 2 \cdot t_r} \left[ 1 - \exp \left[ -\frac{\ln 2 \Delta t}{T_{\frac{1}{2}}} \right] \right] \]

\( t_r \) is the real time during measurement.

\( K_3 \) is the correction factor due to self-attenuation, in the measured sample compared to calibration sample.

\[ K_3 = \frac{1 - e^{-\mu x}}{\mu x} \]
where \( x \) is the thickness of the measured sample and \( m \) is the photon linear attenuation coefficient for the \( \gamma \) - ray energy of interest. If the calibration and the measured samples have the same matrix, then \( K_3 = 1 \).

\( K_4 \) is the correction factor for pulses loss due to random summing. \( K_4 \) is count rate dependent and is given by:

\[
K_4 = \exp(-2R\tau)
\]

\( \tau \) is the resolution time, \( R \) is the mean count rate.

Finally, \( K_5 \) represents the coincidence correction factor for those nuclides decaying through a cascade of successive photon emissions. If the nuclide has no cascade of gamma rays and both calibration source and measured sample contain the same nuclide, then \( K_5 = 1 \) such that:

\[
K_5 = \frac{\varepsilon_{\text{ap}}(E)}{\varepsilon(E)}
\]

The coincidence correction factor \( K_5 \) is defined as the corresponding ratio apparent efficiency \( \varepsilon_{\text{ap}} \) to the full energy peak \( \varepsilon \), obtained from the full energy curve, or SWORD (Monte Carlo model), measured with single photon emitting radionuclides.
Appendix D

Uncertainty propagation in γ-ray spectrometry

Table D.1 shows some of the most important contributions to uncertainty in γ-spectrometry it must be noted these are only illustrative and used as an example.

| Uncertainty       | Source                    | Typical Uncertainty Range (%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission probability</td>
<td>0.1 - 11</td>
<td></td>
</tr>
<tr>
<td>Counting</td>
<td>0.1 - 20</td>
<td></td>
</tr>
<tr>
<td>Attenuation</td>
<td>0.1 - 5</td>
<td></td>
</tr>
<tr>
<td>Half-life</td>
<td>0.01 –1</td>
<td></td>
</tr>
<tr>
<td>Coincidence correction</td>
<td>1 - 15</td>
<td></td>
</tr>
<tr>
<td>Detection efficiency</td>
<td>1 – 5</td>
<td></td>
</tr>
<tr>
<td>Radiochemistry</td>
<td>1-10</td>
<td></td>
</tr>
<tr>
<td>Sample weight</td>
<td>0.01- 1</td>
<td></td>
</tr>
</tbody>
</table>

The sources of standard uncertainties can be grouped according to their origin into 4 categories:

- from preparation of test portion
- from energy and efficiency calibration
- from the measurement of test portion
- from the nuclear data

In most cases the quantity of interest (the measurand) is not the quantity that can be directly measured. Its value has to be derived from values of several other quantities. The combined standard uncertainty of the quantity of interest (the measurand, y) could be derived by applying the “error propagation law” of Gauss.

Quantified by y, \( U_c(y) \) is calculated in terms of component uncertainties, \( U(x_i) \), as follows:

\[
U_c(y(x_1, \ldots, x_n)) = \left( \sum_{i=1}^{m} \left( \frac{\partial y}{\partial x_i} \right)^2 (u(x_i))^2 \right)^{1/2},
\]

Where \( y(x_1, \ldots, x_n) \) is a function of several quantities, \( x_1, \ldots, x_n \). Each variable’s contribution is just the square of the associated uncertainty expressed as a standard deviation multiplied by the square of the associated partial derivative.
Appendix E

Matrix code for fission production analysis and photographs of ‘Sir Robin’ and ‘Bart’

Matrix code originally written by Andy Pearce and adapted for this study.

```
% This program uses the matrix method discussed in "Algebraic approach to
% the radioactive decay equations
% L. Morala and A. F. Pacheco". It was written originally by Andy Pearce
% and then adapted
% to include longer chains (up to 10 long), branching chains and varied
% initial distribution of radionuclei
%
clc;
% zero time, excel days
tzero=0;
% start of decay, excel days
tstart=1;
%This model is for a chain of up to 10 radionuclei. In the matrix Lambda
%log(2)/halflife in seconds for each radionuclide in the chain. When you
%need no
%more radionuclei, set the remaining values to 0
lamba=[ log(2)/0.114;
       log(2)/0.377;
       log(2)/25.1;
       log(2)/(10.3*60);
       log(2)/(64.02*24*3600);
       0;
       0;
       0;
       0;
       0];
A=zeros(10); %initiates a 10x10 all zeros matrix

% Then populate the matrix with the decay constants as shown in the paper
% by Moral and Pacheco with one modification: the lamba values of all
% elements to the
% left of the diagonal are entered, not just those immediately 1 to the
% left of the diagonal.
A(1,:)=[-lamba(1) 0 0 0 0 0 0 0 0];

for i=2:10
    for j=1:i-1;
       A(i,i)=-lamba(i);
       A(i,i-j)=lamba(i-j);
    end
```

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end

% add in branching
B=zeros(10); % the branching is encoded as follows, the diagonal is always 1 (unless the % element is stable in which case it is 0) and then move towards the left, % filling in the ratio of that radionuclide that will decay (e.g. line 3 % says % radionuclide 3 decays (diagonal is 1) and when radionuclide 2 decays it % decays 100% % to radionuclide 3 (term 3 in the row is 1).
B(1,:) = [1 0 0 0 0 0 0 0 0 0];
B(2,:) = [1 1 0 0 0 0 0 0 0 0];
B(3,:) = [0 1 1 0 0 0 0 0 0 0];
B(4,:) = [0 0 1 1 0 0 0 0 0 0];
B(5,:) = [0 0 0 1 1 0 0 0 0 0];
B(6,:) = [0 0 0 0 1 1 0 0 0 0];
B(7,:) = [0 0 0 0 0 1 1 0 0 0];
B(8,:) = [0 0 0 0 0 0 1 1 0 0];
B(9,:) = [0 0 0 0 0 0 0 1 1 0];
B(10,:) = [0 0 0 0 0 0 0 0 1 1];

% element by element multiplication: this integrates the branching % information and decay constant information to produce a new matrix A, % which will take the part of Matrix A as listed in Moral and Pacheco C = A.*B;
A = C;

[V,D]=eig(A); % V = eigen vectors, D = eigen functions

% set initial number of atoms of each radionuclide present.
N0=[1000000000000;10000000000;1000000000000;1000000000000;10000000000000;100000000000000;1000000000000000;10000000000000000;100000000000000000;0 ;0;0;0;0;0;0;0];

% take i steps through the program (if you change this i, change the one in % the next for structure as well to match).

% for i=1:4511 % number of steps
  t(i)=1000*i; % the multiplication here is the size of each time step in seconds.
  L=diag(exp(diag(D).*t(i))); % this line combines equations 6 and 7 from the paper.
  % '.' means element by element multiplication. This is equation 7 from the paper
  % 'diag' uses diagonal matrix as a vector. This is equation 6 from the paper
  N(i,:)=V*L*inv(V)*N0;
end

% output the values to a matrix for plotting
% for i=1:4511
%  for j=1:10
%    N(i,j)=N(i,j)*lambda(j);
%  end
end
\% Plot the activities
\% 
semilogy(t,A(:,1), 'Color', [1, 0.25, 0.25]); \% red
hold on
semilogy(t,A(:,2), 'Color', [0, 0.75, 0]); \% green
hold on;
semilogy(t,A(:,3), 'Color', [0.528, 0.448, 0.9]); \% light purple
hold on
semilogy(t,A(:,4), 'Color', [0.4275, 0.711, 0.720]); \% aqua
hold on
semilogy(t,A(:,5), 'Color', [1, 0.549, 0]); \% orange
hold on
semilogy(t,A(:,6), 'Color', [0.792, 0.882, 0.999]); \% lilac
hold on
semilogy(t,A(:,7), 'Color', [0.969, 0.6916, 0.7334]); \% pink/salmon
hold on
semilogy(t,A(:,8), 'Color', [0.616, 0.820, 0.200]); \% light green
hold on
semilogy(t,A(:,9), 'Color', [0.396, 0.336, 0.765]); \% dark purple
hold on
semilogy(t,A(:,10), 'c-'); \% cyan
hold on
\%axis([0,7500,0.01,1000000000000]); \%This line can fix the axis of the
\%plot. Format is [xmin,xmax, ymin, ymax]

\% 
\% Plot the number of atoms of each radionuclide
\% 
figure(2);
plot(t,N(:,1), 'Color', [1, 0.25, 0.25]); \% red
hold on
plot(t,N(:,2), 'Color', [0, 0.75, 0]); \% green
hold on;
plot(t,N(:,3), 'Color', [0.528, 0.448, 0.9]); \% light purple
hold on
plot(t,N(:,4), 'Color', [0.4275, 0.711, 0.720]); \% aqua
hold on
plot(t,N(:,5), 'Color', [1, 0.549, 0]); \% orange
hold on
plot(t,N(:,6), 'Color', [0.792, 0.882, 0.999]); \% lilac
hold on
plot(t,N(:,7), 'Color', [0.969, 0.6916, 0.7334]); \% pink/salmon
hold on
plot(t,N(:,8), 'Color', [0.616, 0.820, 0.200]); \% light green
hold on
plot(t,N(:,9), 'Color', [0.396, 0.336, 0.765]); \% dark purple
hold on
plot(t,N(:,10), 'c-'); \% cyan
hold on
\%axis([0,7500,0.01,1000000000000]); \%This line can fix the axis of the
\%plot. Format is [xmin,xmax, ymin, ymax]
Figure E.1- Photograph of ‘Bart’ detector, showing distance to source geometry.

Figure E.2- Photograph of ‘Sir Robin’ well detector, showing source geometry inside the well.
Appendix F

NPL UKAS certificates of standards used in the work

NATURAL URANIUM SOLUTION

FOR: 
National Physical Laboratory
Hampton Road
Teddington
TW11 0LU

FOR THE ATTENTION OF: 
Mr Richard Lucas

NPL IDENTIFICATION: 
B11111

DESCRIPTION: 
A radioactive solution of $^{234}$U, $^{235}$U and $^{238}$U in uranyl nitrate in an aqueous solution of 8 mol dm$^{-3}$ nitric acid.

DATE OF CALIBRATION: 
26 September 2011 to 11 November 2011

MEASUREMENTS

Aliquots of B11111 were gravimetrically dispensed to a series of plastic liquid scintillation vials for assay by gamma spectrometry. The samples were counted at two distances on two detectors and activities for $^{234}$U and $^{235}$U calculated. The results were corrected for differences in self-attenuation and volume in comparison with the calibration samples caused by the high density of the uranyl nitrate solution. Aliquots were also dispensed to a mixing bottle along with aliquots of a standardised $^{232}$U yield tracer and the activity of $^{238}$U determined by alpha spectrometry. The ratio of $^{235}$U to $^{238}$U was also confirmed by alpha spectrometry. The $^{235}$U result was determined solely by gamma spectrometry, the $^{238}$U result from a mean of the alpha and gamma spectrometry data and the $^{238}$U result by assuming a ratio of 1:1 with $^{234}$U in natural uranium.

Reference: 201100049-1

Date of Issue: 11 November 2011
Signed: \( \text{Authorised Signatory} \)

Cheked by: \( \text{Dr A V Harms} \) on behalf of NPL ML
RESULTS

Principal radionuclides: $^{234}$U, $^{235}$U, $^{238}$U

Reference time: 2011-11-01 12:00 UTC

Activity concentration of $^{234}$U:
1147 Bq g$^{-1}$

Expanded uncertainty: $\pm 38$ Bq g$^{-1}$ (±3.4 %)

Activity concentration of $^{235}$U:
54.8 Bq g$^{-1}$

Expanded uncertainty: $\pm 1.8$ Bq g$^{-1}$ (±3.4 %)

Activity concentration of $^{238}$U:
1147 Bq g$^{-1}$

Expanded uncertainty: $\pm 30$ Bq g$^{-1}$ (±2.6 %)

NOTES

[1]. The reported reference time is stated consistent with the format given in ISO 8601:2004. UTC is the abbreviation for Universal Time, Coordinated. The date is expressed in the format year-month-day, such that 2008-10-01 represents 1 October 2008.

[2]. The recommended half lives of $^{234}$U, $^{235}$U and $^{238}$U are 8.967 (44) × 10$^7$ days, 2.571 (8) × 10$^9$ days and 1.6319 (36) × 10$^{12}$ days respectively and are derived from the evaluations of the Decay Data Evaluation Project, see for example www.nucleide.org/DDEP.htm.

[3]. The isotopic ratios determined are broadly consistent with those expected from natural uranium. The material assayed had undergone chemical separation, therefore some but not all of the natural series decay progeny are present.

UNCERTAINTIES

The reported uncertainties are based on standard uncertainties multiplied by a coverage factor $k = 2$, providing a level of confidence of approximately 95 %. The uncertainty evaluations have been carried out in accordance with UKAS requirements.
NATIONAL PHYSICAL LABORATORY
Teddington Middx UK TW11 0LW Telephone +44 20 8977 3222
Certificate of Calibration
LEAD-210 STANDARD SOLUTION
B150139

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provides capability of measurement to the SI system of units and/or to units of measurement realised at the National Physical Laboratory or other recognised national metrology institutes. This certificate may not be reproduced other than in full, except with the prior written approval of the issuing laboratory.

FOR: National Physical Laboratory
Hampton Road
Teddington
TW11 0LW
United Kingdom

FOR THE ATTENTION OF: Dr Steven Judge

NPL PRODUCT CODE: R22-02-2015040378-1

SAMPLE IDENTIFICATION: B150139

DESCRIPTION: A radioactive solution of $^{210}\text{Pb}$ as lead nitrate in an aqueous solution of 2 mol dm$^{-3}$ nitric acid also containing 50 μg g$^{-1}$ Pb and 50 μg g$^{-1}$ Bi carrier. The solution is contained in a bottle.

DATES OF CALIBRATION: 11 May 2015

MEASUREMENTS

The samples were prepared by gravimetric dilution of a $^{210}\text{Pb}$ solution, which had been previously standardised by the CIEMAT/NIST efficiency tracing technique. The dilution factor was validated using Liquid Scintillation counting. The presence of gamma emitting contaminants was checked using high-resolution gamma spectrometry.

Reference: 2015040378-1

Date of Issue: 12 May 2015

Checked by: L.V.

Name: Mr A K Pearce
on behalf of NPLML

Signed: (Authorised Signatory)
RESULTS

Principal radionuclide: $^{210}\text{Pb}$

Reference time: 2014-03-01 12:00 UTC

Activity per unit mass of principal radionuclide: 363.8 Bq g$^{-1}$

Expanded uncertainty: $\pm 7.6$ Bq g$^{-1}$ ($\pm 2.1\%$)

Contaminants present: None detected

NOTES

[1]. The reported reference time is stated consistent with the format given in ISO 8601:2004. UTC is the abbreviation for Universal Time, Coordinated. The date is expressed in the format year-month-day, such that 2008-10-01 represents 1 October 2008.

[2]. The recommended half-life of $^{210}\text{Pb}$ is 8120 (100) days and is derived from the evaluations of the Decay Data Evaluation Project, see for example www.nucleide.org/DDEP.htm.

[3]. The nominal mass of solution is 466 g.

[4]. The bottle was dispensed into forty four flame sealed glass ampoules with sample identification A150253 to A150296.

UNCERTAINTIES

The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95%. The uncertainty evaluation has been carried out in accordance with UKAS requirements.
Certificate of Calibration

THORIUM-232
LOW-LEVEL STANDARDS

DESCRIPTION:
A solution of Th(NO₃)₄ in dilute HNO₃
in a 10ml flame sealed British Standard glass
ampoule.

PARAMETER MEASURED:
Activity concentration of ²³²Th, ²²⁴Ra and ²³⁵Th

DATE OF CALIBRATION:
01-20 March 1999

RESULTS
Source Identifier:
Ampoules E450499 to E4589/99

Principal Radioisotope:
Thorium-232

Reference time:
12:00 GMT 20 March 1999

Activity concentration of ²³²Th:
10.716 Bq/g
± 1.91 %

Activity concentration of ²²⁴Ra:
10.716 Bq/g
± 1.91 %

Activity concentration of ²³⁵Th:
10.716 Bq/g
± 1.91 %

Reference: R1946
Date issued: 28 May 1999
Checked By: N. M. Woods
Signed: (Authorised Signatory)

This certificate provides traceability of measurement to recognised national standards, and to the units of measurement used in the NPL or other recognised national standards laboratories. This certificate may only be published in full, unless permission for the publication of an approved extract has been obtained in writing from the Managing Director. It does not in itself indicate the subject of calibration any attributes beyond those above by the data contained herein.

Page 1 of 2

320
NATIONAL PHYSICAL LABORATORY
Continuation Sheet

UNCERTAINTIES

The reported uncertainties are based on standard uncertainties multiplied by a coverage factor k=2, providing a level of confidence of approximately 95%. The uncertainty evaluations have been carried out in accordance with UKAS requirements.

MEASUREMENTS

A solution of $^{229}$Th in radioactive equilibrium with its daughter products was assayed by gravimetric techniques for $^{229}$Th content and by high resolution gamma-ray spectrometry for the gamma emitting daughter radionuclides using a previously calibrated gamma-ray spectrometer.

CONTAMINANTS

Gamma-ray emitting contaminants: None

Alpha emitting contaminants: Not assayed
Mixed Radionuclide

National Physical Laboratory
Hampton Road
Teddington
TW11 0LW
United Kingdom

FOR THE ATTENTION OF: Dr Steven Judge

NPL PRODUCT CODE: R08-04

DESCRIPTION: A mixed radionuclide solution containing americium-241, cadmium-109, cobalt-57, cerium-139, chromium-51, tin-113, strontium-85, caesium-137, manganese-54, zinc-65, cobalt-60 and yttrium-88 as chlorides in 4 mol dm⁻³ hydrochloric acid. The carrier concentration is approximately 50 µg g⁻¹ of each of the above elements, except americium. The solution is contained in a bottle.

SAMPLE IDENTIFICATION: B160110

DATES OF CALIBRATION: 12 April 2016

INTENDED USE: For the calibration of gamma spectrometers

STORAGE: The material may be stored at room temperature in a suitably sealed container. Flame-sealed glass ampoules are recommended for long-term storage. Regulatory conditions may apply to the manner in which this material is stored.

Reference: 2016040164-1
Date of Issue: 4 May 2016
Checked by: [Signature]
Name: Dr J C J Dean

Page 1 of 3

Authorised Signatory on behalf of NPLML
MEASUREMENTS

The samples were prepared by gravimetric dilution of a solution containing a mixture of the radionuclides concerned, the components of which had been previously standardised in a manner traceable to national standards of radioactivity. Gamma emission rates per gram of solution were confirmed using a hyperpure Ge gamma spectrometer that had been previously calibrated in a manner traceable to national standards of radioactivity. The accuracy of the dilution factor was checked using liquid scintillation counting.

RESULTS

Reference time: 2016-06-01 12:00 UTC

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Activity Concentration /Bq g⁻¹</th>
<th>Gamma Energy /eV</th>
<th>Gamma Emission Rate per Unit Mass /s⁻¹ g⁻¹</th>
<th>Gamma Emission Probability /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>²³⁴Am</td>
<td>514.9 ± 6.4</td>
<td>59.5409 ± 0.0002</td>
<td>184.9 ± 2.9</td>
<td>35.92 ± 0.34</td>
</tr>
<tr>
<td>¹⁰⁹Cd</td>
<td>2860 ± 110</td>
<td>88.0336 ± 0.0002</td>
<td>104.7 ± 4.8</td>
<td>3.66 ± 0.10</td>
</tr>
<tr>
<td>⁶⁰Co</td>
<td>108.0 ± 1.5</td>
<td>122.06065 ± 0.00024</td>
<td>92.4 ± 1.3</td>
<td>85.51 ± 0.12</td>
</tr>
<tr>
<td>¹⁰⁹Ce</td>
<td>134.4 ± 2.7</td>
<td>165.8575 ± 0.0022</td>
<td>107.4 ± 2.1</td>
<td>79.90 ± 0.08</td>
</tr>
<tr>
<td>⁵¹Cr</td>
<td>2170 ± 30</td>
<td>320.0835 ± 0.0008</td>
<td>214.7 ± 3.1</td>
<td>9.89 ± 0.04</td>
</tr>
<tr>
<td>¹³⁵Sn</td>
<td>340.8 ± 4.8</td>
<td>391.698 ± 0.0006</td>
<td>221.4 ± 3.3</td>
<td>64.97 ± 0.34</td>
</tr>
<tr>
<td>⁶⁰Sr</td>
<td>419.6 ± 5.8</td>
<td>514.0048 ± 0.0044</td>
<td>413.3 ± 6.6</td>
<td>98.5 ± 0.8</td>
</tr>
<tr>
<td>¹³⁷Cs</td>
<td>574.4 ± 8.0</td>
<td>661.657 ± 0.006</td>
<td>488.2 ± 7.2</td>
<td>84.99 ± 0.40</td>
</tr>
<tr>
<td>⁵⁶Mn</td>
<td>529.3 ± 3.9</td>
<td>834.838 ± 0.010</td>
<td>529.2 ± 3.9</td>
<td>99.9752 ± 0.0010</td>
</tr>
<tr>
<td>⁹⁰Y</td>
<td>508.1 ± 3.8</td>
<td>898.036 ± 0.008</td>
<td>476.1 ± 4.7</td>
<td>93.7 ± 0.6</td>
</tr>
<tr>
<td>⁶⁵Zn</td>
<td>1102 ± 15</td>
<td>1115.539 ± 0.004</td>
<td>553.3 ± 8.0</td>
<td>50.22 ± 0.22</td>
</tr>
<tr>
<td>⁶⁰Co</td>
<td>614.2 ± 8.7</td>
<td>1173.228 ± 0.006</td>
<td>613.3 ± 8.7</td>
<td>99.85 ± 0.06</td>
</tr>
<tr>
<td>⁶⁰Co</td>
<td>614.2 ± 8.7</td>
<td>1332.492 ± 0.008</td>
<td>614.1 ± 8.7</td>
<td>99.9826 ± 0.0012</td>
</tr>
<tr>
<td>⁸⁶Y</td>
<td>508.1 ± 3.8</td>
<td>1836.052 ± 0.026</td>
<td>504.8 ± 3.7</td>
<td>99.346 ± 0.050</td>
</tr>
</tbody>
</table>

UNCERTAINTIES

The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor \( k = 2 \), providing a coverage probability of approximately 95%. The uncertainty evaluation has been carried out in accordance with UKAS requirements.
HALF-LIFE DATA

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life /days</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{241}$Am</td>
<td>158900 ± 440</td>
</tr>
<tr>
<td>$^{199}$Cd</td>
<td>461.9 ± 0.8</td>
</tr>
<tr>
<td>$^{57}$Co</td>
<td>271.80 ± 0.10</td>
</tr>
<tr>
<td>$^{138}$Ce</td>
<td>137.641 ± 0.040</td>
</tr>
<tr>
<td>$^{51}$Cr</td>
<td>27.704 ± 0.008</td>
</tr>
<tr>
<td>$^{112}$Sn</td>
<td>115.09 ± 0.06</td>
</tr>
<tr>
<td>$^{85}$Sr</td>
<td>64.850 ± 0.014</td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>10976 ± 60</td>
</tr>
<tr>
<td>$^{54}$Mn</td>
<td>312.19 ± 0.06</td>
</tr>
<tr>
<td>$^{60}$Zn</td>
<td>244.01 ± 0.18</td>
</tr>
<tr>
<td>$^{60}$Co</td>
<td>1925.2 ± 0.6</td>
</tr>
<tr>
<td>$^{85}$Y</td>
<td>106.63 ± 0.10</td>
</tr>
</tbody>
</table>

NOTES

[1]. The reported reference time is stated consistent with the format given in ISO 8601:2004. UTC is the abbreviation for Universal Time, Coordinated. The date is expressed in the format year-month-day, such that 2008-10-01 represents 1 October 2008.

[2]. The recommended nuclear data are derived from the evaluations of the Decay Data Evaluation Project, see for example www.nucleide.org/DDEP.htm

[3]. The nominal mass of solution is 160.3 g.

[4]. The bottle was dispensed into six flame sealed glass ampoules of type designated in section 3.2 of BS EN ISO 9187-1:2003 as ampoule ISO 9187-2-OPC-I-10-cl, with sample identification A160256 to A160270.

UNCERTAINTIES

The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95%. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

Reference: 2016040164-1

Checked by: [Signature]
NATIONAL PHYSICAL LABORATORY
Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

Certificate of Calibration

RADIUM-226
B150769

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provides traceability of measurement to the SI system of units and/or to units of measurement realised at the National Physical Laboratory or other recognised national metrology institutes. This certificate may not be reproduced other than in full, except with the prior written approval of the issuing laboratory.

FOR: National Physical Laboratory
Hampton Road
Teddington
Middlesex
United Kingdom

FOR THE ATTENTION OF: Dr Steven Judge

NPL PRODUCT CODE: R36-02-2015080223-1

SAMPLE IDENTIFICATION: B150769

DESCRIPTION: A radioactive solution of 226Ra as radium dichloride in an aqueous solution of 1 mol dm$^3$ hydrochloric acid. The solution is contained in a bottle.

DATE OF CALIBRATION: 19 August 2015

MEASUREMENTS

The samples were prepared by gravimetric dilution of a standardised solution of the radionuclide. The solution was standardised using a high-pressure re-entrant secondary standard ionisation chamber previously calibrated for the radionuclide concerned by absolute counting techniques. The accuracy of the dilution factor was checked using liquid scintillation counting. The presence of gamma-ray emitting contaminants was checked using high-resolution gamma spectrometry.

Reference: 2015080223-1

Date of Issue: 4 September 2015
Checked by: P

Signed: A

Name: Mr A K Pearce

Page 1 of 2

(Authorised Signatory)
on behalf of NPLML
RESULT

Principal radionuclide: $^{228}$Ra

Reference time: 2014-02-28 12:00 UTC

Activity per unit mass of principal radionuclide: 101.7 Bq g$^{-1}$

Expanded uncertainty: $\pm 2.5$ Bq g$^{-1}$ (± 2.5 %)

Contaminants present: none detected

NOTES

[1]. The reported reference time is stated consistent with the format given in ISO 8601:2004. UTC is the abbreviation for Universal Time, Coordinated. The date is expressed in the format year-month-day, such that 2008-10-01 represents 1 October 2008.

[2]. The recommended half life of $^{228}$Ra is 5.844 (50) x 10$^7$ days and is derived from the evaluations of the Decay Data Evaluation Project, see for example www.nucleide.org/DDEP.htm.

[3]. The nominal mass of solution is 199 g.

[4]. The bottle was dispensed into nineteen flame sealed glass ampoules with sample identification A150692 to A150710.

[5]. The solution is deemed to be in equilibrium at time of certification.

UNCERTAINTIES

The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.
URANIUM-236 SOLUTION

B140132

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FOR:
National Physical Laboratory
Hampton Road
Teddington
Middlesex
TW11 0LW

FOR THE ATTENTION OF:
Steven Judge

NPL IDENTIFICATION:
B140132

DESCRIPTION:
A radioactive solution of $^{238}$U as uranium (IV) nitrate in an aqueous solution of 2 mol dm$^{-3}$ nitric acid. The solution is contained in a glass bottle.

DATES OF CALIBRATION:
5 November 2013 to 6 October 2014

MEASUREMENTS

The samples were prepared by gravimetric dilution of a standardised solution of the radionuclide. The stock solution was standardised using 4x liquid scintillation counting. The presence of gamma emitting contaminants was checked using high-resolution gamma spectrometry. The presence of alpha emitting contaminants was checked by alpha spectrometry of an electrodeposited aliquot of the solution.

Reference: 2014070149-1

Date of Issue: 7 October 2014

Signed: (Authorised Signatory)

Checked by: Mr A K Pearce on behalf of NPLML
RESULTS

Principal radionuclide: $^{235}\text{U}$
Reference time: 2014-01-01 12:00 UTC
Activity concentration of principal radionuclide: 10.109 Bq g$^{-1}$
Expanded uncertainty: ± 0.048 Bq g$^{-1}$
Contaminants detected: $^{235}\text{U}$
Activity concentration of $^{235}\text{U}$: 0.00050 Bq g$^{-1}$ ± 0.00030 Bq g$^{-1}$

NOTES

[1]. The reported reference time is stated consistent with the format given in ISO 8601:2004. UTC is the abbreviation for Universal Time, Coordinated. The date is expressed in the format year-month-day, such that 2008-10-01 represents 1 October 2008.

[2]. The recommended half lives of $^{235}\text{U}$ and $^{236}\text{U}$ are 2.571 (8) × 10$^{11}$ days and 8.558 (44) × 10$^{8}$ days respectively and are derived from the evaluations of the Decay Data Evaluation Project, see for example www.nucleide.org/DDEP.htm.

[3]. The original mass of solution in B140132 was 109.82 g.

[4]. The bottle was dispensed into ten flame sealed glass ampoules with sample identification A140754 to A140763.

UNCERTAINTIES

The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor $k=2$, providing a coverage probability of approximately 95%. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

Reference: 2014070149-1
Checked by: [Signature]

Page 2 of 2
PLUTONIUM-242 SOLUTION
B160132

FOR:
National Physical Laboratory
Hampton Road
Teddington
TW11 0LW

FOR THE ATTENTION OF:
Lynsey Keightley

NPL IDENTIFICATION:
B160132

DESCRIPTION:
A radioactive solution of $^{242}$Pu in an aqueous solution of 2 mol dm$^{-3}$ nitric acid. The solution is contained in a bottle.

DATE OF CALIBRATION: 20 May 2016

MEASUREMENTS
The sample was prepared by gravimetric dilution of a standardised solution of the radionuclide. The activity per unit mass of the solution was measured by 4π liquid scintillation counting. The presence of gamma emitting contaminants was checked using high-resolution gamma spectrometry and the presence of alpha emitting contaminants was checked using alpha spectrometry.
RESULTS

Principal radionuclide: $^{243}$Pu

Reference time: 2016-04-01 12:00 UTC

Activity per unit mass of principal radionuclide: 1.0759 Bq g$^{-1}$

Expanded uncertainty: ± 0.0046 Bq g$^{-1}$

Contaminants detected:

$^{241}$Am

Activity per unit mass of $^{241}$Am: 0.00316 Bq g$^{-1}$ ± 0.00078 Bq g$^{-1}$

Other contaminants present$^{[2]}$:

$^{241}$Pu

Activity per unit mass of $^{241}$Pu$^{[3]}$: 0.0488 Bq g$^{-1}$ ± 0.0012 Bq g$^{-1}$

NOTES

[1]. The reported reference time is stated consistent with the format given in ISO 8601:2004. UTC is the abbreviation for Universal Time, Coordinated. The date is expressed in the format year-month-day, such that 2008-10-01 represents 1 October 2008.

[2]. The activity per unit mass of $^{241}$Pu was not measured at NPL and is inferred from the certificate for the raw material; as such it is not covered by UKAS accreditation.

[3]. The nominal mass of the solution is 229.0 g

[4]. The recommended half-lives are given in the table below.

<table>
<thead>
<tr>
<th>Radiouclide</th>
<th>Half-life /days</th>
<th>Data Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>Expanded</td>
<td></td>
</tr>
<tr>
<td>$^{241}$Pu</td>
<td>5234 ± 30</td>
<td>DDEP</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>158000 ± 440</td>
<td>DDEP</td>
</tr>
<tr>
<td>$^{242}$Pu</td>
<td>$1.362 \times 10^8$ ± $0.022 \times 10^8$</td>
<td>DDEP</td>
</tr>
</tbody>
</table>

Half-lives are derived from the following data sources: DDEP - Decay Data Evaluation Project, see technical note LNHB 2011/53, CEA, Saclay; IAEA – technical reports STI/PUB/1287 and STI/PUB/1618, IAEA, Vienna; ENSDF - Evaluated Nuclear Structure Data File, published in Nuclear Data Sheets.

UNCERTAINTIES

The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95%. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

Reference: 2016050165-1

Checked by: [Signature]
THORIUM-229 STANDARD SOLUTION
B131361

NATIONAL PHYSICAL LABORATORY
Toddington
Middlesex
UK
TW11 0LW
Telephone +44 20 8977 3222

Certificate of Calibration

FOR:
National Physical Laboratory
Hampton Road
Teddington
Middlesex
TW11 0LW
United Kingdom

FOR THE ATTENTION OF:
Lynsey Keightley

NPL PRODUCT CODE:
R26-01-2013120068-1

SAMPLE IDENTIFICATION:
B131361

DESCRIPTION:
A radioactive solution of $^{229}$Th as thorium nitrate in an aqueous solution of 2 mol dm$^{-3}$ nitric acid also containing 10 µg g$^{-1}$ ammonium cerium nitrate.

DATES OF CALIBRATION:
20 May 2013 to 9 December 2013

MEASUREMENTS

The samples were prepared by gravimetric dilution of a standardised solution of the radionuclide. The solution was standardised using the Triple- to Double- Coincidence Ratio (TDCR) technique and the activity validated by comparison with previous standards. The solution was assayed for radionuclidd impurities by both alpha and gamma spectrometry.

Reference: 2013120068-1

Date of Issue: 9 December 2013

Signed: [Signature]

(Authorised Signatory)

Checked by: [Signature]

Name: Mr A K Pearce

on behalf of NPLML
RESULTS
Principal radionuclide: \(^{229}\text{Th}\)
Reference time: 2013-08-01 12:00 UTC
Activity concentration of principal radionuclide: 10.14 Bq g\(^{-1}\)
Expanded uncertainty: ± 0.14 Bq g\(^{-1}\) (± 1.4 %)
Contaminants present: None detected

NOTES
[1]. The reported reference time is stated consistent with the format given in ISO 8601:2004. UTC is the abbreviation for Universal Time, Coordinated. The date is expressed in the format year-month-day, such that 2008-10-01 represents 1 October 2008.
[2]. The recommended half-life of \(^{229}\text{Th}\) is 2.88 \((10) \times 10^6\) days and is derived from E. Brown and J. K. Tuli, *Nuclear Data Sheets* 109 (2008) p. 2657.
[3]. The nominal mass of solution is 285 g.
[4]. The bottle was dispensed into twenty-seven flame sealed glass ampoules with sample identification A13985 to A131011.

UNCERTAINTIES
The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor \(k = 2\), providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.
Certificate of Calibration

POLONIUM-209 SOLUTION
B140390

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provides credibility of measurement to the SI system of units and/or to units of measurement realised at the National Physical Laboratory or other recognised national metrology institutes. This certificate may not be reproduced other than in full, except with the prior written approval of the issuing laboratory.

FOR:
National Physical Laboratory
Hampton Road
 Teddington
TW11 0LW

FOR THE ATTENTION OF:
Lynsey Knightley

NPL IDENTIFICATION:
B140390

DESCRIPTION:
A radioactive solution of 209Po as polonium chloride in an aqueous solution of 6 mol dm⁻³ hydrochloric acid. The solution is contained in a flame sealed glass ampoule.

DATE OF CALIBRATION:
28 July 2014 to 5 September 2014

MEASUREMENTS

The solution was standardised using 4π liquid scintillation counting and gravimetrically diluted. The accuracy of the dilution factor was checked by liquid scintillation counting. The presence of gamma emitting contaminants was checked using high-resolution gamma spectrometry. The presence of alpha emitting contaminants was checked using alpha spectrometry.

Reference: 2014080362-1

Date of Issue: 21 October 2014

Signed: [Signature]
(Authorised Signatory)

Checked by: [Signature]
Name: Mr S M Jerome
on behalf of NPLML
RESULTS

Principal radionuclide: $^{209}$Po

Reference time: 2014-09-01 12:00 UTC

Activity per unit mass of principal radionuclide: 10.30 Bq g$^{-1}$

Expanded uncertainty: ± 0.18 Bq g$^{-1}$

Contaminants present: none detected

NOTES

[1]. The reported reference time is stated consistent with the format given in ISO 8601:2004. UTC is the abbreviation for Universal Time, Coordinated. The date is expressed in the format year-month-day, such that 2008-10-01 represents 1 October 2008.

[2]. The nominal mass of the solution is 198.35 g.

[3]. The recommended half-lives used are given in the table below.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Half-life /days</th>
<th>Value</th>
<th>Expanded uncertainty</th>
<th>Data Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{209}$Po</td>
<td></td>
<td>42000</td>
<td>± 10000</td>
<td>(i)</td>
</tr>
</tbody>
</table>

Half-lives are derived from the following data sources:

(i) DDEP - Decay Data Evaluation Project, see technical note LNHB 2011/53, CEA, Saclay;
(ii) IAEA - technical reports STI/PUB/1287 and STI/PUB/1618, IAEA, Vienna;
(iii) ENSDF - Evaluated Nuclear Structure Data File, published in Nuclear Data Sheets.

[4]. Polonium has the potential to form complexes and colloids of unpredictable behaviour; therefore to maintain the stability of the solution it is recommended this material is stored and manipulated only in suitably prepared laboratory glassware and that any containers are gently agitated prior to opening and dispensing.

UNCERTAINTIES

The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor $k=2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.
Appendix G

Literature review of other cross section data from $^{236}\text{Np}$ production

When considering deuteron irradiation of $^{238}\text{U}$ (Bellido et al, 1993; Guzhovskii et al, 1994; Lessler et al, 1966; Wing et al, 1959), a similar picture emerges. However there appears to be a sharper peak in the $^{238}\text{Np}$ formation cross-section, and the energy window for the $^{236}\text{Np}$ formation is increased by ~5 MeV, when compared with proton irradiation. There do appear to be some discrepancies between the published data given in Figure G9.1. There is an expected increased angular momentum associated with the $^{238}\text{U}(d,4n)^{236}\text{Np}$ reaction (Bellido et al, 1993) compared to the proton induced reaction on the same target. The peak production cross-section for the deuteron-induced reaction is reported to be approximately 60 mb at a beam energy of 27 MeV, suggesting that this may be the most favourable reaction for the production of a $I^g=6$ $^{236}\text{Np}$ tracer. However this reaction can form $^{237}\text{Np}$ via $(d,n)$ reaction
Figure G9.1 - Activation cross sections for $^{238}\text{U}(d,\text{xn})^{(240-\alpha)}\text{Np}$
Uranium-236 Irradiations

The irradiation of $^{236}$U ($T_{1/2}$: $23.43(6) \times 10^6$ years, DDEP) is compromised by the availability of the nuclide in a suitably pure state. However, consistent results have been obtained for proton irradiation (Aaltonen, et al, 1996; Aaltonen, et al, 2005). The data appears consistent and there are some similarities between this data and that for $^{238}$U in that the cross sections for the $(p,n)$ reaction is $\sim 10$-$15$ millibarns. Although the $(p,3n)$ reaction is not considered in this paper, the maximum of the cross section is $\sim 25$ MeV which is also similar to that for the same reaction in $^{238}$U.

![Uranium-236 irradiation with deuterons](image)

Figure G9.2– Activation cross sections for $^{236}$U$(d,xn)^{(238-x)}$Np
Figure G9.3– Activation cross sections for $^{236}\text{U}(p,xn)^{237-8}\text{Np}$

**Uranium-235**

There appears to be no reported data for proton irradiation of $^{235}\text{U}$ (apart from fission) and the deuteron data (Bellido, *et al.*, 1993; Lessler, *et al.*, 1966; Wing, *et al.*, 1959) appears somewhat inconsistent, as shown in Figure A9.4. It can be seen that there appears to be a peak at around 15 MeV for the $(d,2n)$ reaction cross section and that the $(d,n)$ cross section could be argued to be flat between 5 and 10 millibarns. However, Efurd *et al.*, (1991) reported the formation of $^{237}\text{Np}$ in their irradiation of $^{235}\text{U}$ and it is assumed that the thickness of their target (~1.3 g/cm$^2$) allowed the $^{235}\text{U}(d,\gamma)^{237}\text{Np}$ radiative capture reaction to take place.
Figure G9.4– Activation cross sections for $^{235}\text{U}(d,xn)^{(237-x)}\text{Np}$
Methods of Np production carried out over the course of this study

The irradiations can be grouped as follows:

- Irradiation of $^{235}$U: The target was 99.89% enriched, so the target material was recovered
- Irradiation of $^{236}$U: The target was 99.74% enriched, so the target material was recovered
- Irradiation of $^{238}$U with either protons or deuterons: There is no requirement to recover the target material from the irradiated target

$^{235}$U(d,n)$^{236}$Np

The target material was 99.74% enriched, so the $^{235}$U had to be recovered, the targets were prepared by compaction of an evaporated solution of uranyl nitrate into an aluminium target substrate, with a thin aluminium cover foil. The target was irradiation with 15 MeV deuterons with a thickness of target (~1.3g/cm$^2$) allowed the $^{235}$U(d,γ)$^{237}$Np radiative capture reaction to take place, initial results indicated that no Np was produced from measurements conducted using γ spectrometry, in addition due to a lack of enriched $^{235}$U, this reaction was not continued.

$^{236}$U(p,n)$^{236}$Np

The target prepared for the proton irradiation was with 1.048g of U$_3$O$_8$ which was compacted into an aluminium substrate, with a thin titanium cover foil. The targets were irradiated for 1h with 30 MeV protons on the 14$^{th}$ August 2013.

The irradiation of $^{236}$U ($T_{1/2} = 23.43(6) \times 10^6$ years, DDEP) is compromised by the availability of the nuclide in a suitably pure state. However, consistent results have been obtained for proton irradiation (Aaltonen, et al, 1996; Aaltonen, et al, 2005) (Figure G9.5). The data appears consistent and there are some similarities between this data and that for $^{238}$U in that the cross sections for the (p,n) reaction is ~10-15 millibarns.
The $^{236}\text{U}$ target was cooled for several months to decrease the activity of short lived fission products. It was dissolved in nitric acid with the neptunium and plutonium fractions isolated and the activity of $^{236}\text{Np}$ and $^{236}\text{Pu}$ measured by $\gamma$ and $\alpha$-spectrometry respectively. The radiochemical recovery of $^{236}\text{Np}$ was 60%, while the $^{236}\text{Pu}$ recovery was determined to be 80% based on the use of $^{239}\text{Np}$ and $^{242}\text{Pu}$ tracer respectively. The neptunium fraction was sealed in 10 mL glass ampoule and counted for 100,000 seconds in the well germanium detector Sir Robin but no evidence for the decay of $^{236}\text{Np}$ was observed. Taking into account the neptunium radiochemical recovery and the detection limit for the measurement a conclusion can be made that the amount of $^{236}\text{Np}$ produced during the $^{236}\text{U}$ irradiation did not exceed 1 Bq. The

Figure G9.5 – Summary of published cross sections for the $^{236}\text{U}(p,xn)^{237-x}\text{Np}$ reactions.
plutonium fraction was electroplated and measured by α-spectrometry. The spectrum is presented in Figure G9.6 and the analysis shows that based on the efficiency correction used 2.1 kBq of $^{236}$Pu was produced at the time of irradiation. The α-decaying ground state of $^{236}$Pu would also be formed in this material via the β-decay of the low-spin, $I^\pi = 1 - ^{236m}Np$ (Ardisson, et al, 1994).

Figure G9.6- Alpha spectra of $^{236}$U(p,n) $^{236}$Np irradiation.
Appendix H

List of publications and conference presentations

The following section includes (for reference) the papers currently published based on this EngD thesis:


The following papers are those based on additional research carried out during the EngD thesis:

Régis, J.-M et al., 2014. $B(E2;2^+_1 \rightarrow 0^+_1)$ value in $^{90}$Kr. Physical Review C 90, 067301.


**Conference Presentations**

The following section outlines all conference presentations carried out during this EngD thesis:

**Target preparation for production of $^{236}$Np**
Coordinating Group on Environmental Radioactivity (COGER), April, 2012, Portsmouth, UK. *Oral.*

**NPL reference material characterisation for 2014 PTE exercise**
NPL Environmental Proficiency Test Exercise 2014, April, 2014, Teddington, UK. *Oral.*

**Progress towards the production of $^{236}$Np**
Institute of Physics (IOP) Nuclear Physics Group Conference, April, 2014, Croydon, UK. *Poster.*

**Progress towards the production of $^{236}$Np standard sources and competing fission fragment production**

**Selection of reference materials for MetroNORM**
8th International Conference on High Levels of Natural Radiation and Radon Areas (ICHLNRRA), September 2014, Prague. Czech Republic, *Oral.*

**Progress on the chemical separation of fission fragments from $^{236}$Np produced by proton irradiation of natural uranium target**

**Destructive and non-destructive measurements of NORM in monazite-rich sands of Brazil**
2nd International Conference on Dosimetry and its Applications (ICDA-2), July 2016, Guildford, Surrey, UK. *Poster.*

**Reference materials produced for a European metrological research project focussing on measurements of NORM**

**Consensus evaluation of radioactivity-in-soil reference materials in the context of an NPL Environmental Radioactivity Proficiency Test Exercise**
International Committee for Radionuclide Metrology Low-Level Measurement Techniques (ICRM-LLMT) September 2016, Seattle, US. *Oral. (Co-author, presented on behalf of main author).*
Destructive and non-destructive measurements of NORM in monazite-rich sands of Brazil. *Radiation Physics and Chemistry*
Appendix I
Peer Reviewed Journal Papers

The following section includes (for reference) the papers currently published because of this EngD:

Progress on the chemical separation of fission fragments from $^{238}$Np produced by proton irradiation of natural uranium target

C. Larjani$^{a,b}$, S.M. Jerome$^c$, G. Lorussoc, P. Ivanovd, B. Russell$,^e$ A.K. Pearce$^f$, P.H. Regan$^{a,b}$

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$^b$ Department of Physics, University of Surrey, Guildford GU2 7XH, UK

A R T I C L E   I N F O

Keywords
Chemical separations
Fission fragments
Mass analysis and neutron activation

A B S T R A C T

The aim of the current work is to develop and validate a radiochemical separation scheme capable of separating both $^{239}$Pa and $^{238}$Pa from a uranium target of natural isotope composition ($1 \pm$ g uranium) and $200 \text{ mg}$ of fission decay products. A target consisting of 1.2 g of U, was irradiated with a beam of 25 MeV protons with a typical beam current of 10 mA for 1.6 h in December 2013 at the University of Birmingham Culham facility. Using literature values for the production cross-section for fission of protons with uranium targets, we estimate that an upper limit of approximately 280 Bq of activity from the $^{239}$Pa ground state was produced in this experiment. Using a radiochemical separation scheme, Np and Pa fraction were separated from the produced fission decay products, with analysis of the target-based final products done using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and high-resolution photon and particle spectroscopy.

1. Introduction

The procedures used in radiochemical separations are rarely fully quantitative. Given it is necessary that an accurate chemical yield is determined for the radionuclide of interest. In order to carry out this, it is necessary to have a way of monitoring the chemical recovery, which can be accomplished by the use of a radiochemical yield tracer. The overall aim of the research is dedicated to producing an ionopure vacuum radioisotope tracer for Np analysis. The choices available for a suitable Np tracer are constrained (Larjani et al., 2017) one can use a Pa yield tracer such as $^{234}$Pa (Jerome et al., 2004). However, with the complex chemistry of the actinide series, there is always the risk of contamination of Pa in Np during the analysis.

The radionuclide $^{234}$Pa has a ground state half-life of 1.55(9)×10$^5$ years (Chechey and Kuzmenko, 2012a) and is of interest as a chemical yield tracer for the radiochemical and mass spectrometric analysis of $^{239}$NP (Larjani et al., 2014b). A long-lived waste product from nuclear reactor operation, arising from the decay of $^{239}$U (t$\text{_{1/2}}$ 423,660 y; Chechey and Kuzmenko, 2010b). Various production mechanisms of $^{234}$Pa involving charged-particle irradiation of uranium targets (Chechey, 2015) or $^{238}$U have been studied, with the proton bombardment of $^{238}$U showing the most promising results in terms of $^{234}$Np production yield and isotopic purity (Jerome et al., 2014). The metastable state $^{234}$Np (t$\text{_{1/2}}$ 22.5(4) h; Chechey and Kuzmenko, 2012b) is also produced in these reactions. The metastable state and ground state of $^{234}$Np both decay to $^{234}$Pa (t$\text{_{1/2}}$ 2.85(8) y; Broome and Tall, 2004) and $^{234}$U (t$\text{_{1/2}}$ 2.34(6)×10$^5$ y; Lomax, 2012). The $^{234}$Pa daughter subsequently decays to $^{234}$U (t$\text{_{1/2}}$ 76,611 y; Percival, 2008), both of which can be used as indirect signatures of the production of $^{234}$Np. The primary challenge in the radiochemical separation of $^{234}$Np from the production target material is to isolate trace amounts of ground state $^{234}$Np (specific activity $\sim$360 M$\text{Bq} \text{ g}^{-1}$) from significant quantities of uranium from the target material and fission products produced during irradiation (Larjani et al., 2015).

The ultimate aim of the current work is to develop and validate a radiochemical separation scheme capable of separating both $^{234}$Np and $^{234}$Pa from a uranium target of natural isotope composition ($1 \pm$ g uranium) and $200 \text{ mg}$ of fission decay products. In the current paper, results for the target and separated fractions are presented, which have been measured using an online high-resolution gamma-ray spectrometry to confirm the production and decay of $^{234}$Np in either the ground state or metastable state, which consolidate our previous paper on this topic (Jerome et al., 2014). The mass distribution of the fission residues created during the target bombardment has been presented previously (Larjani et al., 2015). Results are also presented for the effectiveness of extraction chromatography (TEVA resin, Triilam International) for the major fission product elements using mixed stable-element standard solutions, with recoveries of the separated fractions measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).
2. Materials and methods

2.1. Target irradiation

A target containing 1.2 g of UO₂ was irradiated with a beam of 25 MeV protons of typical beam current of 30 μA at the University of Birmingham Cyclotron facility. The target was produced by compacting natural uranium dioxide at 60 kN cm⁻² into an aluminium target holder and a 0.025 mm tantalum foil, which was then subjected to a proton irradiation for a total duration of 19 h over a period of 3 days (9–11th December 2013). Directly following the irradiation, the target was left to cool for approximately 20 days, allowing the short-lived fission products to decay. The radiochemical processing of the target was carried out at NPL in February 2014 with the irradiated target being dissolved in 10 M nitric acid, with the concentration adjusted to 8 M and transferred into an AstIon bottle before proceeding with further work. A 1 g aliquot (of the 1.2 g target material dissolved in 8 M nitric acid weighing a total of 40.21 g) of the solution was dispensed into a 2 ml glass British Standard (BS795:1983) ampoule for measurement by γ-ray spectrometry.

2.2. Estimate of the initial 239+240Pu production yield

The current work used the fusion-evaporation reaction 238Pu(p,3n)236Pu at a proton energy of 25 MeV, to form the final residual nucleus of interest.

The estimated production of 236Pu in the current study can be determined using the relation,

\[ R = \sigma \cdot \phi \cdot n \]

where:
- \( R \) is the number of 236Pu atoms formed per second per unit volume (s⁻¹ cm⁻³)
- \( \sigma \) is the production cross section (units in cm²)
- \( \phi \) is the particle flux per unit area (cm⁻² s⁻¹)
- \( n \) is the number of target atoms per unit volume (cm⁻³)

The particle flux per unit area is not known in detail since the cross-section of the beam was not well established, however, since the stated beam current was delivered to the entire target, then we can assume:

\[ \frac{R_{236Pu}}{\sigma \cdot \phi \cdot n_{236Pu}} \approx \tau \]

where \( R_{236Pu} \) is the total number of product atoms (236Pu) formed, \( n_{236Pu} \) is the total particle flux (s⁻¹), and \( \tau \) is the total irradiation time, (18.72 h = 67 900 s in this case).

The total number of target atoms irradiated is then \( n_{238Pu} = \frac{n_{236Pu}}{M_{236Pu}} \cdot M_{238Pu} \cdot n_{236Pu} \), where \( n_{238Pu} \) is the mass of the target, \( M_{238Pu} \) is the molecular mass of the target compound (g mol⁻¹), \( M_{236Pu} \) is the number of moles of the element of interest per mole of the target compound (dimensionless), and \( n_{236Pu} \) is the abundance of the isotope of interest in that element (dimensionless), with \( Na \) being Avogadro’s constant.

Thus we obtain the relation for the total number of produced 236Pu atoms (neglecting any decay during the irradiation period) of:

\[ R_{236Pu} = \sigma \cdot \frac{1}{\phi} \cdot \left( \frac{M_{238Pu} \cdot M_{236Pu} \cdot n_{236Pu}}{M_{238Pu}} \right) \]

where for this particular production experimental production run, \( \sigma = 55.3 \times 10^{-27} \text{cm}^² \) is the estimated production cross-section of 238Pu via the 238Pu(p,3n)236Pu nuclear reaction (using the PACE IV fusion evaporation code) and \( \phi = 30 \times 10^{12} \text{cm}⁻² \cdot \text{s}⁻¹ \).

This leads to a value of \( n_{236Pu} = 9 \times 10^{14} \) atoms.

Also, \( n_{238Pu} = 2.2 \) g of UO₂ in the production target, with \( M_{238Pu} = 270.03 \text{ g mol}⁻¹ \), \( M_{236Pu} = 1.6 \), \( \beta = 0.99928 \) which leads to:

\[ \frac{R_{236Pu}}{\sigma} = \frac{1.2 \times 6.022 \times 10^{23} \times 1 \times 0.99928}{270.03} = 7 \times 10^{10} \text{ g} \]

This leads to an (upper limit) estimate of the total production of 238Pu (i.e. in both the ground and metastable states) in this experiment of approximately 1.7 × 10¹⁴ atoms, which is equivalent to a 238Pu mass of approximately 7 × 10⁻¹⁴ g.

This number of atoms would result in a maximum value for the activity from the 238Pu ground state (\( q_{238Pu} = 3.55 \times 10^{10} (\text{g} \cdot \text{cm}⁻³) \)) of approximately 250 Bq.

When considering the production of 239Pu, the formation ratio of 238Pu to 239Pu must also be considered. This is not well established and is also likely to be production-reaction dependent, but has been estimated to be less than 1-6 in previous literature (Hambach et al., 1985; Ehrler et al., 1991; Gindler and Stohler, 1999) in favour of the high-spin ground state. This is likely to be of this order or even larger with the use of a fusion-evaporation reaction which are well known to preferentially populate near-yield, high-spin states in the residual decay. This gives a useful estimate of the total amount of 239Pu tracer that was created in the target irradiation, which was available for extraction and measurement of the characteristic decay properties, following different chemical separations to attempt to preferentially select the 239Pu tracer from other decay products, target material and fission decay products, which were also produced in significant quantities in the target irradiation following the proton-induced fission of 238U (Larjani et al., 2015).

2.3. Radiochemical separation

The proposed separation procedure for 239Pu from an irradiated target can be divided into three stages:

1. Removal of the target matrix, UO₂:

   This was achieved by dissolution of uranium in nitric acid, followed by extraction of uranium into diethyl ether (Curran et al., 1955); diethyl ether specifically extracts uranium from nitric acid solutions, leaving all other elements in the aqueous phase, although there is a limited solubility of the aqueous phase in the ether phase and vice versa, necessitating additional extractions (see Fig. 1).

2. Isolation of neptunium:

   Although neptunium displays a number of oxidation states, the Np⁴⁺ ion is not stable in acid solution and may be oxidised to Np⁷⁺ in the presence of nitric acid. However, the Np³⁺ ion is retained by TEVA extraction chromatography resin (Jarowicz et al., 1959); in 2.5 M HNO₃, the Np³⁺ ion has a distribution coefficient (K) of ~8
and may be stabilised by reduction with ascorbic acid in the presence of the ferric ion, Fe(III) (Strikvolski et al., 2013). Under the same conditions, the $k_m$ for Pu($^{244}$) is ~0-0000. No significant retention of the major fission products by TEVA resin from 2.5 M HNO₃ was observed during the method validation work; therefore the fission products have been removed from the column by rinse with 20 mL of 2.5 M nitric acid solution as shown in Fig. 2; however, the very high levels of fission products > 50 Mq, depending on cooling time, necessitate additional clean-up of the separated neptunium.

2. Isolation of neptunium:

Furthermore, it is possible to selectively elute $^{239}$Pa from the TEVA resin by reduction of Pu($^{244}$) to Pu($^{242}$) by rinsing the column with 20 mL of 9 M HCl containing 0.1 M of NH₄ prior to stripping $^{239}$Np by washing with 10 mL of 0.1 M HCl (see Fig. 1).

Prior to testing with the target material, the procedures were tested for a simulated fission product solution using stable element standards (Zr, Nb, Mo, Ru, Rh, La, Ce, Sm), with recoveries from each stage assessed by ICP-MS.

3. Experimental techniques

3.1. Gamma-ray spectrometry

The LN2 cooled high purity germanium (HPGe) γ-ray spectrometer 'Lanexdet' which is semi-planar HPGe detector with a carbon fibre detector window and a relative (to a 3''×3'' NaI(Tl) detector) efficiency of ~65% was used to perform a series of measurements of the prepared sample. The fractions were measured for a typical counting time of 250,000 s in September 2016, just under 3 years after the initial irradiation, resulting in the decay of the shorter-lived fission products that were measured in Larijani et al. (2015). The net peak areas of the discrete γ-ray emissions associated with specific fission fragment decays were calculated using the Canberra Genie 2000 v2.1c software (see Fig. 2).

A 1 g fraction ampoule following Np extraction was also measured using a HPGe well detector, which is shown in Fig. 3, in which the region associated with characteristic peaks associated with the direct decay of the $^{236}$Np ground state to excited states in $^{230}$U are highlighted.

3.2. Alpha-spectrometry

The sources prepared by electroplating from a pH adjusted sulphuric acid solution (Hallardus, 1984) were counted in an ORTEC Octet Plus 0-particle spectrometer with Passivated Implanted Planar Silicon (PIPS) detectors and ORTEC Master Multi-channel Analyzer (MCA) application software. The energy calibration of the detectors was performed with a $^{241}$Am, $^{244}$Cm and $^{239}$Np source. The sources were counted for 70,000 s, in a geometry with an estimated counting efficiency of 21.5% based on the solid angle coverage. The instrumental backgrounds were measured prior to the sample measurement.

Fig. 4 shows an example of the various spectra measured in the current work, with the characteristic decays from the ground state of $^{232}$Pa particularly evident.

3.3. Inductively Coupled Plasma Mass-Spectrometry (ICP-MS)

In addition to the separated $^{239}$Np and $^{239}$Pa samples, mixed stable element standards were measured using an Agilent 8800 triple quadrupole (ICP-QQQ-MS) to assess the stable element composition. The instrument is equipped with two quadrupole mass filters, separated by an octopole collision-reaction cell. It was fitted with a quartz double-pass spray chamber, MicroMist nebuliser, nickel sample and skimmer cones. The instrument was operated in single quadrupole mode throughout (i.e. with only one mass filter operating), and tuned daily using a mixed 1 μg g$^{-1}$ standard solution. Calibration standards were also prepared for $^{248}$Pu, $^{244}$Np, $^{244}$Cm, $^{239}$Pu and $^{235}$Pu to assess instrument sensitivity. The measurement time was approximately

![Fig. 2. Gamma-ray spectra to show the effects of the various stages of the chemical separation scheme on the target material. These data were taken on samples 2 years and 6 months after the initial target irradiation, measured for 250,000 s.](image2.png)

![Fig. 3. Gamma-ray spectrum of a g of the initial target fraction following the neptunium separation, as measured in the well HPGe detector. The live time for this spectrum was 2.1×10$^6$ s.](image3.png)
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is the main directly populated state in the electron capture of $^{236}$Np, the subsequent transitions in the γ-ray decay cascade are all rather highly converted with total internal conversion coefficients of $\alpha_{\text{int}} = 1.8, 1.1$ and 0.04 for the 160.3, 104.2 and 45 keV transitions to $^{236}$U respectively (Xibell, 2008).

The γ-ray spectrum displayed in Fig. 2 shows transitions associated with decays from fusion-product decay chains with half-lives of the order of a year or more, such as $^{125}$Sb, $^{125}$Te, $^{125}$Xe, $^{125}$Xe, $^{125}$Te and $^{125}$Te. The comparable γ-ray spectrum for the same separated nuclides from 1000 g of the major component of these materials can be removed/reduced in this spectrum compared to the target material fraction.

Fig. 3 shows the γ-ray spectrum from the separated Np fraction as measured in a HPGe well detector which had an increased sensitivity for low-energy γ rays and higher overall full-energy peak detection efficiency compared to "Lancet". In addition to the fission fragments, lines are also evident in the target fraction spectrum which are associated with the decay chains of members of the Thorium (4n) natural decay series. These are created in the target following the α decay of $^{235}$U to $^{231}$U and its subsequent decay to $^{231}$Pa which decays down the traditional 4n series terminating at $^{231}$Pa. Notably, some of these α decay lines from the 4n series are also identified in the α-particle spectrometry part of this work (see Fig. 4).

The main difference between the Np fraction to the unseparated target fraction is the relative increase in the intensity of the K-shell X-ray close to 80 keV. These could arise from the Np electron capture branch, but are also possible emissions following internal conversion from excited states populated in the U, Pa daughters.

4.1. Methodology for determination of the $^{236}$Np content

The decay of the long-lived, high-spin coupling ground state in $^{236}$Np ($^{236}$Np) proceeds by both $\beta^-$ decay to $^{236}$Pa and by electron capture to $^{236}$U (Brown and Tuli, 2006) with branching ratios of approximately 13% and 86.3% respectively. The metastable excited state in $^{236}$Np ($^{236}$Np) decays by $\beta^-$ and electron capture to $^{236}$Pu and $^{236}$U respectively. The branching ratios for these competing decay branches from $^{236}$Np are listed as 50(3) % for each decay mode in the most recent nuclear data evaluation (Brown and Tuli, 2006).

To guide this analysis, Fig. 5 shows calculated ground state and decay curves using the standard laws of radioactive decay for the decays associated with the decay and feeding from the $t_{1/2} = 1.55 \times 10^3$ year $^{234}$Np ground state and $t_{1/2} = 22.5(4)$ h metastable state.

4.1.1. Using γ rays from the 86% electron capture branch

The most direct signature of $^{236}$Np is the detection of γ rays from the $6^+ \rightarrow 4^+ \rightarrow 2^+ \rightarrow 0^+$ cascade in $^{236}$U, populated by the electron-capture branch of the $^{236}$NP decay ($\approx 86.3\%$). This cascade results in the emission of γ rays of energy 160, 104, and 45 keV, (see Table 1), (Brown and Tuli, 2006). In this experiment, detection of these discrete energy signature γ rays is complicated by the γ-ray background produced by the large quantity of fission products generated by $^{252}$Cf$(p,f)$ reactions. Although the $\gamma^*$ excited state in $^{236}$U state...

4.1.2. Time dependence of the $^{236}$Pa activity and extrapolated $^{236}$Pu production at production time zero

In the current analysis, the clean signature of the α decay of $^{236}$Pa (see Fig. 4) ($t_{1/2} = 2.858(6)$ years (Brown and Tuli, 2006)) could be detected. From the chemical separations conducted to isolate Pa, the signature energy peaks from the α decay of $^{236}$Pa are 5720.87 (10) keV and 5767.53 (8) keV with an intensity of 20.83% (3) and 69.15% (2) respectively (Brown and Tuli, 2006). There is no mechanism of making $^{236}$Pa ($Z = 94$) directly in the reaction ($\alpha$, $\gamma$) and therefore we attribute the presence of Pa in the sample to stem from the $\beta^-$ decay of $^{236}$Np or $^{236}$Pa. Due to the isomeric state half-life of 22.5(4) hours, all $^{236}$Np would have decayed within the target prior to the
chemical separation procedure, accounting for the vast majority of the $^{239}$Pu in the sample. As Fig. 5 shows, this is, by far, the largest contribution to the total amount of $^{239}$Pu even assuming a reduced isomeric isomer ratio due to the factor $6 \times 10^4$ difference in the half-lives of the metastable state and ground state in $^{239}$Np.

4.1.2.1. Estimated $^{239}$Pu production: at effective time zero based on a-spectrometry. An analysis was carried out using $1/4$ of the total dissolved target material, with a sub-sampling of the target material taken for a-particle spectrometry being 0.020(4) g. The α measurements were performed prior to any chemical separation and therefore no correction is required for separation recovery.

Table 1

<table>
<thead>
<tr>
<th>Neptunium-239 g</th>
<th>1.65$\times$10$^9$ years</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Half life</strong></td>
<td>$\pm$ Energy (keV)</td>
</tr>
<tr>
<td><strong>Decay transitions</strong></td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>315</td>
</tr>
<tr>
<td><strong>Electron capture</strong></td>
<td>620</td>
</tr>
<tr>
<td></td>
<td>791</td>
</tr>
<tr>
<td>γ</td>
<td>44.63</td>
</tr>
<tr>
<td></td>
<td>45.344</td>
</tr>
<tr>
<td></td>
<td>56.4</td>
</tr>
<tr>
<td></td>
<td>102.82</td>
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<td></td>
<td>104.1</td>
</tr>
<tr>
<td></td>
<td>104.333</td>
</tr>
<tr>
<td></td>
<td>158.35</td>
</tr>
<tr>
<td></td>
<td>340.10</td>
</tr>
<tr>
<td></td>
<td>518.1</td>
</tr>
<tr>
<td></td>
<td>594.5</td>
</tr>
<tr>
<td></td>
<td>642.34</td>
</tr>
<tr>
<td></td>
<td>687.39</td>
</tr>
</tbody>
</table>
Table 2

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life</th>
<th>Characteristic α-decay energies (keV)</th>
<th>α-decay intensity (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>238U</td>
<td>2.349(3)</td>
<td>415(8) (10)</td>
<td>35% (3)</td>
<td>Bowman et al. (2007)</td>
</tr>
<tr>
<td>232Th</td>
<td>1.05(5)</td>
<td>41.54 (10)</td>
<td>77% (8)</td>
<td>Tull (2006)</td>
</tr>
</tbody>
</table>

In order to determine the 234Pu activity, A0, from the original target material at effective time zero, we use the measured 239Pu total activity three years after the irradiation and the decay half-life of 2.838(8) years +0.9(5)%,

Estimating the geometrical counting efficiency of α-particle spectrometry to be 24(5)% and using the counts measured associated with the 249Pu α-particle emissions at 5720.357 (10) keV and 5767.53 (8) keV (relative intensities of 30.8% (5) and 61.5% (5)% respectively) (see Table 2) we measured 6.66 × 10^{-10} counts in the Pu region of interest over a counting time of 70,000 s. This corresponds to a lower limit estimate of the total target activity associated with 239Pu of 8(3) × 10^{-10} Bq at the time of measurement and 1.5(5) × 10^{-10} Bq at the time of production.

Taking into account the half-life of 2.838(8) years for 239Pu, leads to a lower limit estimate for the total number of 239Pu atoms produced following decay of 239Np α=10^{-10} Bq at the time of measurement and 1.5(5) × 10^{-10} Bq at the time of production.

4.1.4. ICP-MS measurement of simulated fission product solutions

A 100 µg/g simulated fission product solution was loaded onto a 2 g pre-packed TENV resin cartridge in 10 mL 2.5 M HNO3 with ascorbic acid in the presence of HNO3, followed by an additional 10 mL wash with the same solution. This was followed by 10 mL of 9 M HCl ~1 M of NHCl and 10 mL of 0.1 M HCl, representing the 238Pu and 239Pu elution fractions, respectively. A 1 mL aliquot of each fraction was diluted to a total volume of 10 mL with 2% HNO3 for ICP-MS measurement, with the recovery assessed by comparing the counts in each fraction to the counts in the load solution. No fission products were detected in the Pu and Np elution fractions, with the detection limit equivalent to a recovery of 0.1%. The recoveries in the load and wash fractions ranged from 44% (Np) to 66% (La), suggesting that there is some retention on the resin, which may be improved by an increased wash volume.

An important consideration for the target sample is the very high activities of fission products (> 50 MBq, depending on cooling time), which affects the performance of the resin column. In the 239Pu and 239Np eluted fractions, the uranium activity was reduced by 3 orders of magnitude compared to the load solution as a result of the 2.5 M HNO3 + ascorbic acid + Pd2⁺ wash, however the U content was still very high, and further separation is required.

The mass resolution of ICP-MS cannot discriminate between 239Pu, 239Pu, and 239Np. However, elevated counts were measured at mass 236 using ~1% of the total dissolved target material, before taking a 239Pu elution fraction, and 239Pu was also detected, suggesting that 239Pu is present. Additionally, high the uranium content, there may be some contribution from 239U, which is based on this timescale would be formed following the decay of 239Np, which would give rise to a similar amount of 239Pu atoms based on its branching ratio. Assuming all counts at mass 236 were from the Np ground state, the activity concentration in the undiluted sample was 2.2 ± 0.1 Bq/g (uncertainty from the counting statistics only).

The results highlight the importance of a more extensive clean-up of the separated neptunium in order to get conclusive results. A procedure has also been developed using a tracked column approach with TENV above TRU resin. The sample loading and Pu elution conditions are the same as previously described, however 239Pu is eluted in 0.2 M HNO3, which is then reused on the TRU cartridge. At this stage the cartridges are separated, and the TRU cartridge is washed with 10 M HCl to remove any fission products that pass through the TENV cartridge. Elution of 239Np is achieved with 1 M HCl combined with 0.1 M hydrochloric acid.

5. Conclusions

A radiochemical scheme has been developed for the separation of Np and Pu from fission fragments, produced as part of the target irradiation of natural uranium. Our spectrometric analysis show that the chemical separation scheme adopted separates Pu from fission fragments and other α-particle emitting radionuclides, including the target uranium material. The results to identify the production of Np are more complicated. The γ-ray spectroscopy used shows the signature γ-ray for the decay of the 239Np ground state 166.3 keV at the minimum detectable activity in the current work. The presence of 239Np characteristic lines in the α-particle spectrometry analysis indicates the production of its 239Pu mother nucleus in the metastable state at a level of at least 4×10^{-10} atoms. The ICP-MS measurement shows an elevated at mass 236, however it was not possible to differentiate between the
isobaric tripeptide $^{232}$U, $^{238}$Pb and $^{238}$Np in the current work. For future work, the complete removal of the co-produced fission products is further development and optimization of the $^{238}$Np separation scheme would be required. The authors are planning to perform method development work based on the application of highly specific extraction chromatography resins such as TRU and TMC, along with the use of vacuum box technology to facilitate the separation process and to allow washing with excessive amounts of rinsing solution intended to remove interfering radionuclides.

Acknowledgement

This work is funded through the UK National Measurement Office (Grant no. 117925). P.I. Regan also acknowledges support from UK Science and Technology Facilities Council (STFC) grant ST/L005783/1.

References


Destructive and non-destructive measurements of NORM in monazite-rich sands of Brazil

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1. Introduction

The Earth and its atmosphere contains a range of Naturally Occurring Radioactive Material (NORM), with minerals and raw materials such as limestone, rutila, zircon, monazite and xenotime containing trace amounts of radionuclides of natural origin (U Th K). There are areas known for their particularly high levels of background natural radiation compared to the global average. These include the coastal regions of Oman in the Oman (Chir et al., 2013), Kerala in India (Sartori et al., 2012), and the monazite sands of the Atlantic coast of Brazil (Sartori et al., 2012), which is the focus of the current study. These locations all have geological and geochemical characteristics which are responsible for elevated levels of natural occurring radioactivity.

In addition to the human health aspects, understanding the activity concentration in areas with particularly high levels of background radiation compared to the world average is important from a micro/astro-biological perspective. There is a notable lack of literature regarding the ionizing radiation dosimetry which arise from Naturally Occurring Radioactive Materials in the microbionomes inhabiting these environments. Such data would provide advances in understanding of the habitability of extra-terrestrial bodies such as Mars where cosmic radiation poses one of the major threats to microbial survival (Borrell et al., 2007).

The beaches of Arris Preta, Matape and Morro which are located in the Guarapari region of the Espirito Santo State, in South-East Brazil, provide a useful environmental setting to test the effects of the radioactive properties of certain elements present within the monazite sands on the local microorganisms. Samples from the three sites were collected, with varying heavy mineral accumulations between them. This short paper will present a preliminary evaluation of the activity concentration of the sand samples from a range of beach locations in Brazil that have been determined for members of the $^{238}$U and $^{232}$Th decay series, as well as the primordial radionuclide $^{40}$K. These measurements have been performed using a combination of destructive and non-destructive techniques, in order to provide data that can be taken forward for future studies in regard to the impact of radiation dose on microbial survivability. The activities can also be used to calculate the associated radiation hazard indices that can be compared to the internationally accepted values set by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR, 2000).

2. Materials and methods

2.1. Sample collection and gamma-ray spectrometric analysis

Samples were collected from the beaches of Arris Preta and Morro
in Guarapari and from Meloá, all in South East Brazil. The samples were selected systematically from the three locations to ensure a reasonable representation of the distribution of the NORM materials in the environment. The removal and collection of the sand samples were taken at depths of 40–50 cm from an area of ~75 cm² at the surface; the samples were then placed in high density polyethylene containers, sealed and numbered. Sand samples were prepared for measurement using a procedure developed in the NEL low-level environmental radioactivity laboratory (Harwood and Gilligan, 2010). All materials were placed into an oven and dried at a temperature of 50°C to remove moisture content; the optimum drying time was estimated by weighing the sample every three hours until a constant weight was observed for at least three successive measurements. The material was then transferred into a suitable container and sieved to 150 μm size mesh. The material was then transferred to 20 ml plastic liquid scintillation vials, sealed with PVC tape and stored for a month (~7 half-lives) to allow for the 208Tl to reach secular equilibrium with its parent 232Th within the 4±2 (uranium) decay series. Examples of the vial-based final samples used for γ-ray spectrometric measurement are shown in Fig. 1.

2.2. Sample digestion prior to Th, U and trace element measurement

For the ICP-MS analysis, the monazite sands were digested using an automated beaker fusion technique using the Katanax RE (Katanax Inc., 2016), utilizing a technique originally developed for concrete in a European Metrology Research Programme (EMRP) titled Metrology for Radioactive Waste Management (URF ENV09). Briefly, 0.5 g of each sand sample was added to a Pt crucible, along with 3 g lithium metaborate, 1.5 g lithium tetraborate, 0.25 g lithium bromide and 0.01 g lithium fluoride. The furnace was ramped up to 1000°C, and the sample did not enter the Katanax until this temperature was reached. The material was fused at this temperature for 10 min. The temperature was then ramped to 1020°C and held for 1 min. Throughout the procedure, the Pt crucibles were rocked to aid the fusion. At the end of the procedure, the crucibles were tipped into PTFE beakers containing 50 ml 20% (v/v) HNO₃ and stirred with a FEP magnet stirrer.

Following dissolution, a 0.1 g aliquot was taken and diluted in 2% HNO₃ for measurement by ICP-MS without any radiochemical separation.

2.3. Experimental techniques

2.3.1. Gamma-spectrometry

A high purity germanium (HPGe) γ-spectrometer ‘Lomocell’ was used to perform a series of measurements on the three prepared samples. This is a semi-planar HPGe detector with a carbon fibre detector window and a relative (to a 3+6 Ge NaI(Tl) detector) efficiency of 63% at 1332 keV (60Co) and resolution of 1.70 keV at 1332 keV (60Co). The sample format was initially ~10 g of sample contained in a centrifuge tube; samples were later sub-sampled into 20 ml plastic LS vials so that activity per unit mass could be accurately determined. Each sample was counted for 50,000 s. To reduce the external γ-ray background in the measured spectrum, a cylindrical lead shield with a fixed bottom and a movable cover shields the detector. The detector is designed for low-background measurements and sits inside a low-background lead shield consisting of an outer layer of 11 cm ‘contemporary’ lead at 500 Bq kg⁻¹ 224Ra and an inner layer of 9 cm aged 16th century lead at 5 Bq kg⁻¹ 226Ra. Lomocell’s carbon fibre layer window allows for the measurement of low energy γ-rays emissions in the NORM samples. The detector operates using a high-voltage power supply, Canberra ART research amplifier with a 6 s shaping time, a multi-channel analyser and utilizes the “FUR/DT” circuitry to correct for pile-up and dead-time counting effects. Spectral data was analysed using Canberra software, while the analysis of full-energy peaks due to energies of interest was carried out using ORF data analysis package from the Radware software suite (Rainford, 1995).

2.3.2. Inductively coupled plasma mass-spectrometry (ICP-MS)

Dissolved samples were measured using an Agilent 7500 triple quadrupole ICP-QQQ-MS to assess the stable element composition (Am et al., 2016). The instrument is equipped with two quadrupole mass filters, separated by an octopole collision-reaction cell, and was fitted with a quadruple-pass spray chamber, MicroMass nebulizer, and nickel sample and skimmer cones. The instrument was operated in a single quadrupole mode throughout (i.e. with only one mass filter operating), and tuned daily using a mixed 1 mg L⁻¹ standard solution. Single element calibration standards were prepared for all elements measured. The measurement time was approximately 5 min per sample, and the instrument background was counted before and after each sample.

2.4. Analysis corrections and activity calculations

2.4.1. SWORD model

Regarding the high resolution γ-spectrometry, two measurement geometries were used; initial measurements were performed with the samples “as received” in polypropylene centrifuge tubes, after which weighed sub-samples were transferred to 20 ml Teflon-coated plastic liquid scintillation vials. In the case of the centrifuge tube measurements, the sample fill level was greater than in the calibration samples so a volume correction was necessary in addition to accounting for the differing matrix. In the case of the scintillation vial-based measurements, care was taken during the transfer process to ensure the sample geometry matched the calibration so only a matrix (density) correction was required. In order to determine these correction factors a Monte Carlo model (Quinn, 2007) of the sample and detector (Table 1 for detector components) was developed using the SWORD version 5 package and executed with the GRANT4 code. The elemental compositions used as input to the model were based on the results of the Scanning Electron Microscope analysis (Fig. 2). Correction factors were determined at each of 15 energy points corresponding to the main gamma energies of the radionuclides in NEL mixed radionuclide calibration source solution (241Am, 209Bi, 237Np, 214Bi, 214Po, 238Pu, 252Cf, 239Pu, 240Pu, 241Am, 241Am) and 108Rh (24), which covers the energy range 60–1856 keV. For intermediate energies an interpolation based on a nonlinear fit to a skewed error function was used. In order to validate the model, the Monte Carlo calculated efficiencies were compared with measured efficiencies, the modelled efficiency of the 241Am 60 keV transition was low by 10% with all other modelled efficiencies being within 5% of the measured values. This could be due to the overestimation of the thickness of one of the “dead layers”
between the detector and the source. This level of agreement was considered sufficient for the purposes of deriving correction factors.

Taking this into consideration, the uncertainty associated with the correction factor was conservatively estimated to be about 15% of the magnitude of the correction; therefore, at energies above 100 keV the uncertainty associated with this correction is small compared with other components such as counting statistics and background.

2.4.2. Activity per unit mass determination

Each of the six samples was measured on "Amesol" for 50,000 s.

An example gamma-ray spectrum from a sample from the Areia Preta location is shown in Fig. 3. The direct measurement of $^{238}$U and $^{232}$Th activities is problematic due to the rather low relative $\gamma$-ray intensities following their decay (Naves, 2016). However, their activities can be estimated via the $\gamma$-ray emissions of their daughter products in their respective decay series under the assumption of secular equilibrium.

![Gamma-ray spectrum from Areia Preta sample](image)

### Table 1

<table>
<thead>
<tr>
<th>Item</th>
<th>Material</th>
<th>Model shape</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detector front window</td>
<td>Carbon fiber</td>
<td>Cylinder</td>
<td>0.08 cm height</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.17 cm radius</td>
</tr>
<tr>
<td>Detector outer case</td>
<td>Carbon fiber</td>
<td>Hallow cylinder</td>
<td>0.98 cm height</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.75 cm inner radius</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.08 cm outer radius</td>
</tr>
<tr>
<td>Detector</td>
<td>Germanium</td>
<td>Cylinder</td>
<td>3.53 cm height</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.03 cm radius</td>
</tr>
<tr>
<td>Detector ballastation</td>
<td>Germanium</td>
<td>Three stacked truncated cones</td>
<td>Radius: 1: 3.75 cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Radius: 2: 1.15 cm at 0.3 cm high</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Radius: 3: 0.33 cm at 0.3 cm high</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Radius: 4: 0.33 cm at 0.3 cm high</td>
</tr>
<tr>
<td>Detector dead layer</td>
<td>Germanium</td>
<td>Part of truncated cone</td>
<td>0.3 cm height</td>
</tr>
<tr>
<td>Control wall</td>
<td>Vacuum</td>
<td>Cylinder</td>
<td>0.68 cm deep</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.48 cm radius</td>
</tr>
<tr>
<td>Control wall and copper</td>
<td>Vacuum</td>
<td>Truncated cone</td>
<td>Radius: 2: 0.24 cm at 0.23 cm high</td>
</tr>
<tr>
<td>Copper liner</td>
<td>Copper</td>
<td>Hallow cylinder</td>
<td>4.66 cm height</td>
</tr>
<tr>
<td>Source mount holder</td>
<td>Polyethylene methacrylate</td>
<td>Hallow cylinder</td>
<td>0.75 cm thick</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.39 cm height</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.69 cm outer radius</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.49 cm thickness</td>
</tr>
</tbody>
</table>

![Gamma-ray spectrum from Areia Preta sample](image)

### Table 2

<table>
<thead>
<tr>
<th>$^{238}$U series radionuclide</th>
<th>Energy (keV)</th>
<th>Emission probability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{214}$Po</td>
<td>2062 (0)</td>
<td>3.6 (0)</td>
</tr>
<tr>
<td>$^{214}$Bi</td>
<td>1764 (0)</td>
<td>13.1 (0)</td>
</tr>
<tr>
<td>$^{214}$Pb</td>
<td>1765 (1)</td>
<td>44.0 (1)</td>
</tr>
<tr>
<td>$^{214}$Th</td>
<td>1094 (2)</td>
<td>14.7 (2)</td>
</tr>
<tr>
<td>$^{214}$Rh</td>
<td>7004 (9)</td>
<td>0.7 (0)</td>
</tr>
<tr>
<td>$^{214}$K</td>
<td>1040 (9)</td>
<td>5.6 (0)</td>
</tr>
<tr>
<td>$^{214}$Th (α, α, 0γ)</td>
<td>14004 (6)</td>
<td>5.6 (6)</td>
</tr>
</tbody>
</table>

(Ravasanzai & et al., 2014). A list of $\gamma$-ray transitions associated with the most significant lines used to determine the activity concentrations of $^{238}$U and $^{232}$Th and their subsequent decay daughters are provided in Tables 2. The activity concentrations of the singly decaying nuclides.

### Table 3

<table>
<thead>
<tr>
<th>Element</th>
<th>% (k=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>42.2 ± 0.8</td>
</tr>
<tr>
<td>Si</td>
<td>29.1 ± 0.6</td>
</tr>
<tr>
<td>Ti</td>
<td>11.4 ± 0.7</td>
</tr>
<tr>
<td>Ca</td>
<td>8.9 ± 0.3</td>
</tr>
<tr>
<td>Mg</td>
<td>4.2 ± 0.2</td>
</tr>
<tr>
<td>Al</td>
<td>3.4 ± 0.3</td>
</tr>
<tr>
<td>Fe</td>
<td>15.1 ± 0.1</td>
</tr>
</tbody>
</table>

![Back-scattered electron image of the Areia Preta sand and its elemental composition](image)

The expected expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor k=2, providing a coverage probability of approximately 95%.
Table 3: Decay scheme of 226Ra, 222Rn and 218Po in radon daughters and their activity concentration in soil samples. (Data taken from Decay Data Evaluation Project (DDEP, 2010), www.nrad.bnl.gov/DDEP.html).

<table>
<thead>
<tr>
<th>226Ra series</th>
<th>Radionuclide</th>
<th>Energy (keV)</th>
<th>Emission probability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>222Rn</td>
<td>332 (3)</td>
<td>13.2 (2)</td>
<td></td>
</tr>
<tr>
<td>218Po</td>
<td>911.7 (4)</td>
<td>28.9 (4)</td>
<td></td>
</tr>
<tr>
<td>221Rn</td>
<td>986.9 (37)</td>
<td>13.8 (2)</td>
<td></td>
</tr>
<tr>
<td>218Po</td>
<td>238.6 (2)</td>
<td>43.3 (3)</td>
<td></td>
</tr>
<tr>
<td>218Po</td>
<td>380.1 (40)</td>
<td>3.3 (4)</td>
<td></td>
</tr>
<tr>
<td>218Po</td>
<td>727.2 (9)</td>
<td>6.48 (4)</td>
<td></td>
</tr>
<tr>
<td>218Po</td>
<td>1420.7 (10)</td>
<td>1.51 (2)</td>
<td></td>
</tr>
<tr>
<td>218Po</td>
<td>2640.2 (2)</td>
<td>20.4 (2)</td>
<td></td>
</tr>
<tr>
<td>218Po</td>
<td>2640.2 (10)</td>
<td>99.8 (4)</td>
<td></td>
</tr>
</tbody>
</table>

Table 4: Elemental composition of sands using ICP-MS. The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor k=2, providing a coverage probability of approximately 95%.

<table>
<thead>
<tr>
<th>Element</th>
<th>Sand 10 Area</th>
<th>Sand 14 Area</th>
<th>Sand 21 Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na (ppm)</td>
<td>89.4 ± 0.1</td>
<td>74.8 ± 0.5</td>
<td>214.8 ± 0.1</td>
</tr>
<tr>
<td>Mg (ppm)</td>
<td>42.3 ± 0.4</td>
<td>129.6 ± 0.3</td>
<td>284.6 ± 0.7</td>
</tr>
<tr>
<td>Al (ppm)</td>
<td>42.8 ± 0.8</td>
<td>279.0 ± 0.5</td>
<td>28.9 ± 0.9</td>
</tr>
<tr>
<td>Ca (ppm)</td>
<td>39.1 ± 0.5</td>
<td>217.2 ± 0.6</td>
<td>35.9 ± 0.8</td>
</tr>
<tr>
<td>Cr (ppm)</td>
<td>3.8 ± 0.1</td>
<td>3.9 ± 0.1</td>
<td>5.7 ± 0.3</td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>46.4 ± 0.4</td>
<td>241.6 ± 0.3</td>
<td>42.2 ± 0.5</td>
</tr>
<tr>
<td>Mn (ppm)</td>
<td>3.8 ± 0.1</td>
<td>3.9 ± 0.1</td>
<td>5.7 ± 0.3</td>
</tr>
<tr>
<td>Hf (ppm)</td>
<td>0.8 ± 0.1</td>
<td>0.8 ± 0.1</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>Zr (ppm)</td>
<td>0.8 ± 0.1</td>
<td>0.8 ± 0.1</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>Sr (ppm)</td>
<td>7.7 ± 0.3</td>
<td>27.3 ± 0.1</td>
<td>32.3 ± 0.3</td>
</tr>
<tr>
<td>Ca (ppm)</td>
<td>308.2 ± 0.5</td>
<td>40.1 ± 0.1</td>
<td>339 ± 0.6</td>
</tr>
<tr>
<td>Cr (ppm)</td>
<td>0.3 ± 0.1</td>
<td>0.4 ± 0.1</td>
<td>0.3 ± 0.4</td>
</tr>
<tr>
<td>Cu (ppm)</td>
<td>0.3 ± 0.1</td>
<td>0.4 ± 0.1</td>
<td>0.3 ± 0.4</td>
</tr>
<tr>
<td>Ba (ppm)</td>
<td>0.3 ± 0.1</td>
<td>0.4 ± 0.1</td>
<td>0.3 ± 0.4</td>
</tr>
<tr>
<td>La (ppm)</td>
<td>0.3 ± 0.1</td>
<td>0.4 ± 0.1</td>
<td>0.3 ± 0.4</td>
</tr>
<tr>
<td>Pb (ppm)</td>
<td>0.3 ± 0.1</td>
<td>0.4 ± 0.1</td>
<td>0.3 ± 0.4</td>
</tr>
</tbody>
</table>

Figure 4: Weighted mean activity concentrations of 40K for sample 14 (see Table 3). The weighted means were computed using individual data points for the calculated activity concentrations of 226Ra, 222Rn and 218Po from the 1460.8 keV line.

40K was determined directly by measurement of the 1460.8 keV line (Cameron and Sing, 2004).

The specific activity, in terms of the activity concentration, is defined as the activity per unit mass of the sample. The specific activity of individual radionuclide in soil samples is given by the following equation:

\[ A = \frac{C_0}{\sqrt{2 \pi m E}} \]

where \( A \) is activity concentration in Bq kg\(^{-1}\), \( C_0 \) is the net count of the corresponding full energy peak, \( m \) is the absolute full-energy peak detection efficiency, \( f_g \) is the emission probability per decay corresponding to the specific \( \gamma \) ray energy, \( f_r \) is the counting time in seconds and \( m \) is the mass of soil sample in kg.

2.4.3. Dose calculations

2.4.3.1. Absorbed dose rate in air (D). A direct connection between radionuclides and their exposure is known as the absorbed dose rate (D) in the air at 1 m above the ground surface, the dose rate is derived in units of mGy h\(^{-1}\), where the mean activity concentrations of 226Ra, 222Rn and 40K in Bq kg\(^{-1}\) are used to determine the absorbed dose in mGy h\(^{-1}\) (Boek, 1972). The coefficients for the following equation have been taken from (UNSCEAR, 2000) report.

\[ D = (0.462 A_{226Ra} + 0.634 A_{222Rn} + 0.0617 A_{40K}) ]

2.4.3.2. Radon equivalent activity (Rn eq). Using the activity concentrations of 226Ra, 222Rn and 40K derived from the measured samples, a common radionuclide index, namely the radon equivalent activity (Rn eq) (Bereczki and Mathews, 1985) can be derived. By determining the Rn eq, the associated radionuclide dose can be determined 1 m above the ground surface (Bereczki and Mathews, 1985; Dragosic et al., 2006).

\[ Rn_{eq}(Bq \text{ kg}^{-1}) = A_{222Rn} + 1.4 A_{226Ra} + 0.077 A_{40K} \]

where \( A_{222Rn} \), \( A_{226Ra} \) and \( A_{40K} \) are the activity concentration of 222Rn, 226Ra and 40K in Bq kg\(^{-1}\).

The calculation is based on the assumption that 370 Bq kg\(^{-1}\) of 226Ra or 259 Bq kg\(^{-1}\) of 222Rn or 4810 Bq kg\(^{-1}\) of 40K produces the same gamma dose rate. The permissible maximum value of the radon equivalent activity is 370 Bq kg\(^{-1}\) (UNSCEAR, 2000) which corresponds to an effective dose of 1 mSv for the general public.

3. Results and discussion

3.1. Stable element composition

The stable element composition of sands sample IDs 10, 14 and K are given in Table 4. Additional composition was measured using scanning electron microscopy (Fig. 3). A future aim is to combine x-ray fluorescence and ICP-MS for measurement of 232Th and 238U. In order to reliably compare results across these techniques, digested samples must undergo chemical separation prior to measurement, with the use of 226Ra and 232Th tracers to assess recovery. Additionally, a greater number of samples must be measured, as a 0.5 g aliquot cannot account for heterogeneity in the samples.

3.2. Specific activity of 238U, 226Ra, 222Rn, 40K and dose assessment

The isotopic activity ratio to determine this equilibrium was calculated from the activity concentration, which was measured using a range of relatively intense x-ray transitions (Tables 2, 3). A range of different spectral lines of the identified daughters from the 226Ra series were used to determine a weighted mean and uncertainty for the # decay chain (Fig. 4). By analysing the signatures from the thorium decay, results are consistent with one another (with a rectangular uncertainty), indicating secular equilibrium has been established by the associated daughter radionuclides in the Area Preta sands.

The results of the 8 Area Preta, Melpo and Moni sands are summarised in Tables 5, 6. The initial x-ray spectrum measurements indicated lower radioactivity in the Melpo and Moni samples than in the Area Preta samples. The analysis was carried out on the 4 Area Preta samples, all showed significantly elevated radioactive content (a
### Table 6

Thorium (40Ar) series results. The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor k=2, providing a confidence probability of approximately 95%.

<table>
<thead>
<tr>
<th>Neucleide</th>
<th>Technique</th>
<th>8Ar</th>
<th>9Ar</th>
<th>10Ar</th>
<th>14Ar</th>
<th>K</th>
<th>Meso</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>Micro</th>
<th>Macro</th>
</tr>
</thead>
<tbody>
<tr>
<td>232Th</td>
<td>ICP-MS</td>
<td>-</td>
<td>1078 ± 5</td>
<td>1426 ± 12</td>
<td>4002 ± 5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>232Th (gt 20Ma)</td>
<td>γ-spectrometry</td>
<td>6830 ± 80</td>
<td>7220 ± 70</td>
<td>3070 ± 40</td>
<td>65 ± 4</td>
<td>82 ± 4</td>
<td>256 ± 13</td>
<td>340 ± 13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>230Th (gt 20Ma)</td>
<td>γ-spectrometry</td>
<td>6130 ± 70</td>
<td>6130 ± 60</td>
<td>3670 ± 30</td>
<td>60 ± 4</td>
<td>82 ± 4</td>
<td>256 ± 13</td>
<td>340 ± 13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>230Th (gt 60Ma)</td>
<td>γ-spectrometry</td>
<td>6490 ± 77</td>
<td>6490 ± 60</td>
<td>3640 ± 30</td>
<td>60 ± 4</td>
<td>82 ± 4</td>
<td>256 ± 13</td>
<td>340 ± 13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>230Th (gt 80Ma)</td>
<td>γ-spectrometry</td>
<td>6530 ± 50</td>
<td>6530 ± 60</td>
<td>3720 ± 60</td>
<td>60 ± 4</td>
<td>82 ± 4</td>
<td>256 ± 13</td>
<td>340 ± 13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 7

Comparison of mean and range values for activity concentrations of 234Th, 232Th, and 238K in beach sands in current study and different areas in the world.

<table>
<thead>
<tr>
<th>Region/Country</th>
<th>234Th (Bq/kg)</th>
<th>232Th (Bq/kg)</th>
<th>238K (Bq/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>Range</td>
<td>Mean</td>
<td>Range</td>
</tr>
<tr>
<td>Edarab, India</td>
<td>12</td>
<td>(6-25)</td>
<td>144</td>
</tr>
<tr>
<td>Ulai, India (Keshavabahal et al., 1986)</td>
<td>12</td>
<td>-</td>
<td>104</td>
</tr>
<tr>
<td>Northeast, Yemen (Essa et al., 1991)</td>
<td>13</td>
<td>(3-19)</td>
<td>102</td>
</tr>
<tr>
<td>West coast, Thailand</td>
<td>-</td>
<td>-</td>
<td>102</td>
</tr>
<tr>
<td>East coast, Thailand</td>
<td>-</td>
<td>-</td>
<td>102</td>
</tr>
<tr>
<td>East coast, Philippines</td>
<td>-</td>
<td>-</td>
<td>102</td>
</tr>
<tr>
<td>Eswatini (Essa et al., 1989)</td>
<td>-</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>New Zealand, Egypt, Egypt (2006)</td>
<td>15</td>
<td>7</td>
<td>214</td>
</tr>
<tr>
<td>Eastern region, Turkey (Onay et al., 2007)</td>
<td>1</td>
<td>52</td>
<td>(21-64)</td>
</tr>
<tr>
<td>World average (UNSCAR, 2005)</td>
<td>2</td>
<td>45</td>
<td>(1-9)</td>
</tr>
<tr>
<td>MetroGEM Sand sample (ISO 11467:1993)</td>
<td>&lt;2</td>
<td>2</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Arica Peru sand sample mean value</td>
<td>112 ± 8</td>
<td>(60-165)</td>
<td>6092 ± 29</td>
</tr>
<tr>
<td>Meso sand sample mean value</td>
<td>&lt;4</td>
<td>&lt;4</td>
<td>69 ± 4</td>
</tr>
<tr>
<td>Macro sand sample mean value</td>
<td>&lt;4</td>
<td>&lt;4</td>
<td>69 ± 4</td>
</tr>
</tbody>
</table>

### Table 8

Data on 22Na and 232Th of Arica Peru sands:

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Na-22 dose rate (Bq/Lh)</th>
<th>Na-22 dose (Bq/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arica Peru sand value</td>
<td>3546</td>
<td>9290</td>
</tr>
<tr>
<td>Meso sand value</td>
<td>48</td>
<td>116</td>
</tr>
<tr>
<td>Macro sand value</td>
<td>66</td>
<td>133</td>
</tr>
<tr>
<td>World-wide range</td>
<td>16-92</td>
<td>&lt;270</td>
</tr>
<tr>
<td>World-wide mean (UNSCAR, 2005)</td>
<td>55</td>
<td>-</td>
</tr>
</tbody>
</table>

background subtracted γ-ray spectrum of one of these samples is shown in Figure 5. The majority of the γ-ray signatures found in this spectrum belong to the 22Na decay chain, direct signatures include 22Ar, 22Na, 214Pb, 214Bi, and 214Po, with additional decay signatures from the 222Rn series (212Rn, 212Po, and 212Bi) and also the 1460 keV line from 232Th.

The highest weighted mean 232Th activity concentration derived from γ-spectrometry in this work was in sample 14 of the Arica Peru sands (Fig. 4). The Arica Peru samples showed a mean value of 6692 ± 29 Bq/kg and a range of 4924–7720 Bq/kg. Significantly higher values than those measured from other sites around the world (Table 5), and more than 100 times higher than the World average of 45 Bq/kg found in the UNSCEAR (2000) report. By comparison, the 238K activity concentrations of the sands was 3 times higher, while the results for 230Ra activity indicate an enrichment of radium in the samples from all three areas. The decay activity of 230Ra was measured directly via the 186 keV transition, in addition to activity concentrations of its subsequent decay daughters further down the chain 228Th and 228Ra. The 238K value obtained was lower than the World average, however the γ decay of 238U at 1460 keV interferes with the γ-ray emission from the decay of 238U at 1460 keV energy line, as a consequence there is an increased uncertainty on the measurement of 238K.

Although the samples from Meso and Macro, did not show the levels of enriched thorium as those samples from Arica Peru with mean activities of samples being 69 ± 4 Bq/kg and 345 ± 12 Bq/kg respectively, the samples from Meso and Macro, were still significantly greater
than World averages for thorium. For U and 40K, the mean sample averages were below the World averaged as reported by UNSCEAR (2000).

Dose and \( R_{n} \) values were derived from the high resolution γ-ray spectrometry measurements (Table 8), with both Cop-MS and radiometric measurements indicating a dominance of \( 226\text{Ra} \) (~1.6% by mass) in the marine sands, which could partially explain the high density of 2.9 g/cm\(^2\) derived from the sands (heavy materials are defined as those with a density above 2.9 g/cm\(^2\)) (IAEA, 2000). The EMRP MacroNorm (JRF INTSYS) sand samples had a density of 1.05 g/cm\(^3\), in this work the increased density can be attributed to the geological makeup of the material such as the high Ti content in the sands as shown by the Scanning Electron Microscope data. The derived values for the Areia Preta sands are ~70 times higher than the world averages for U and ~25 times higher for the \( R_{n} \) measurements. Likewise, the Macro were ~2 times and ~1.5 times higher for both dose and \( R_{n} \) measurements, respectively. However, the Marbele sands were within the Worldwide ranges set out by UNSCEAR (2000).

Heavy metals such as molybdenum occur in mineral sand placer deposits and in veins, or are disseminated predominantly in alkaline intrusions in hard rock (Van Groen and Lowen, 2007). The IAEA (2003) derived a value for molybdenum tailings of between 1500 and 50,000 Bq/kg for 237Np and 239-245, for \( 137\text{Cs} \), of which the values found in this work fall into this range.

4. Conclusions

The results obtained from this study display the presence of both members of the 137\text{Cs} and 137\text{Tb} decay series. The samples from the Areia Preta region were found to be the most radioactive and were highly enriched in thorium. Radiometric secular equilibrium has been displayed for the 238U daughter radionuclides and the specific activities for 226Rn, 228Rn and \( 137\text{Cs} \), together with their associated radiological risk factors, have been evaluated. The samples from Areia Preta and Marbele show results much higher than the world averages provided by UNSCEAR (2000), and are many orders of magnitude more radioactive than corresponding sand measurements carried out from various areas previously.

Acknowledgements

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References


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Reference materials produced for a European metrological research project focusing on measurements of NORM


1. Introduction

The global environment is radioactive due to the presence of long-lived radionuclides of uranium and thorium which make up much of the World’s naturally occurring radioactive material (NORM) (Koschorke, 1998). In general, most human exposure to NORM does not result in radiation doses significantly greater than typical background levels of the order of a few millisieverts per year (UAEA, 2003). However, processing of minerals and raw materials may concentrate or distribute NORM. When such materials are being handled or processed, it is necessary to determine the makeup of the radionuclides present and their specific activities in order to assess the risk to health which they represent. The European Metrology Research Programme (EMRP) project IND07 (MetroNORM) seeks to address some of the measurement challenges by investigating present state-of-the-art and suggesting improvements and novel developments for:

- reference materials and sources,
- in situ measurement systems and sampling methods,
- standardisation and development of measurement procedures,
- improvements of NORM related nuclear decay data, and
- on-site and in situ testing of the measurement procedures.

This paper is concerned with MetroNORM work package 1 (reference materials and sources) and the measurements carried out at NPL to certify these materials as reference standards. The need for environmental radioactivity solid reference materials is driven by the requirement for quality control materials for traceability, method validation and instrument calibration. The sample preparation, material characteristics via γ, α and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and the assignment of values for both the 234U (Thoreon) and 238U (Thorium) decay series are described.
2. Materials and methods

2.1. Selected reference materials

NPL and their partners in the project selected and analysed the following candidate materials:

- Coal ash (mining and combustion industries)
- TiO₂ waste/residues (paint pigment)
- Tuff (building industry in Italy)
- Shale (MeSO₄) (cracking and waste water industry)
- Sand oil mixture (oil and gas industry)

Each material was assayed by γ-spectrometry and radiochemical analysis that included a spectrometry measurements for α emitting uranium and thorium isotopes (such as 238U and 232Th). Based on the availability and activity concentration from the measurements, the final 3 candidate reference materials selected by NPL for use in the project were TiO₂, tuff and sand as outlined in the following subsections.

2.1.1. TiO₂ waste

Titanium dioxide is a simple inorganic compound commercially produced as a white powder. It is commonly available in two main crystal forms, ilmenite and rutile (IAEA, 2011) and typically supplied to the market in a range of package sizes or in bulk. The material is used as a white pigment in paints and plastics, although none of the NORM activity transfers to the titanium dioxide products (IAEA, 2011). The majority of the input activity transfers to the processing wastes which need to be managed properly, prior to disposal. Processing of TiO₂ bearing raw materials may generate scale deposits and other wastes that may contain increased radiocaesium levels. The material obtained in this study is from a TiO₂ processing facility in the Czech Republic, was supplied NPL with 10 kg of un-dissolved raw material waste from processing that had been carried out in 2014.

2.1.2. Tuff

Tuff (from the Italian tuffo) is a type of rock made of volcanic ash ejected from a vent during a volcanic eruption which is also used as building material. The material selected in this work is from the Gulf of Naples area in Italy, which is home to Mount Vesuvius. NPL were provided with 5 kg of tuff by a commercial supplier in Italy in order to carry out analysis on the material.

2.1.3. Sand

The sand samples used in the project originated from the petroleum exploration industry. The samples were selected systematically from a variety of locations in Kuwait to ensure accurate representation of the distribution of the NORM materials in the environment. The removal and collection of the sand samples were taken at depths of 5-25 cm from an area of ~175 cm² at the surface; the samples were then placed in containers, sealed and numbered.

2.2. Sample preparation

On receipt, the tuff, TiO₂ and sand samples were prepared for measurement in the NPL low level environmental radioactivity laboratory (Harms and Gilligan, 2010). All materials were dried to constant weight in an oven to eliminate all moisture content; samples were weighted every three hours, and drying was considered to be complete when a constant weight was observed for more than three successive measurements. The material was then transferred into a suitable container and sieved to 150 μm mesh. The material was then transferred into a Turbulin 181 mixer, and bottled for analysis. All of the samples were measured instead of measuring a randomly selected subset of samples. The between sample variance was determined by measuring all of the samples of each reference material once by high-resolution γ-spectrometry, while the measurement variance was determined by measuring a single sample of each material 10 times (Harms and Gilligan, 2010). The homogeneity uncertainty, umax, was calculated as the square root of the difference between the between-sample variance, σ²(batch), and either:

- the measurement variance, σ²(meas), or
- the squared mean of the counting uncertainties, σ²(counts) (whichever was greater).

The homogeneity uncertainties for tuff, sand and TiO₂ were 0.9%, 1.1% and 1.3% respectively (ISO guide 35: 2006).

2.3. Radiochemical separation of Th and U for α-particle and mass spectrometry measurement

The reference materials are solid complex matrices requiring dissolution in order to carry out radiochemical separations to isolate the radionuclides of interest. Prior to dissolution, each sample was spiked with calibrated isotope dilution tracers, ²³²Th and ²³²Th, for both α-particle spectrometry and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) measurements.

The selected dissolution technique for tuff and sand was a conventional hydrofluoric acid dissolution using a microwave oven, while the TiO₂ underwent Lithium Borate fusion, using a KBr crucible, and then a 2.5% HCl for leaching. After dissolution the samples were separated and isolated with the use of USEPA pre-packed columns (Fleming, 1991). Each elemental fraction was then prepared for α-particle spectrometry and ICP-MS.

2.4. Experimental techniques

2.4.1. Gamma spectrometry

A high purity germanium (HPGe) γ-spectrometer ‘Lancet’ was used to perform a series of measurements on the three prepared samples (Harms and Gilligan, 2012). This is a semi-planar HPGe detector with a carbon fibre detector window and a relative (to a 2 x 2 in NaI(Tl) detector) efficiency of 63%. The sample format was ~120 g of the matrix contained in a 125 ml Alron bottle. To reduce the external γ ray background in the measured spectrum, a cylindrical lead shield with a fixed bottom was used inside the detector to shield the detector. Each sample was assayed twice using a semi-planar germanium γ-spectrometer. Counting times for each sample was 50,000 s and the detector was calibrated for the individual radionuclides using standards of ²²⁴Ra, natural uranium, ²³⁵U and ²³⁵U. A calibration curve was also derived based on measurements of an NPL mixed radionuclide solution (R08-03) in the same geometry.

The activity was calculated using like-for-like calibration factors for ²³³Th, ²³²Th, ²³³Th, ²³²Th and ²³⁵U. In the case of the decay product of ²²⁴Ra, measurement of the ²²⁴Ra → ²²⁴Th decay chain was used to derive the ²²⁴Ra activity. The decay chain may be compromised potentially by losses of ²²⁴Ra (as might be expected from outgassing) and therefore calibration factors were derived based on the mixed radionuclide standard via a measured calibration curve. Only γ rays that were not subject to cascade summing were used to calculate activity values (see Table 1).

In order to transform the efficiency derived using aqueous standards to that of the sample (tuff, TiO₂ or sand), a GIANT 4 model (see Fig. 1) was developed using SWORD v5.6 (Goeke, 2007). The elemental compositions used as input to the model were based on the results of the Scanned Electron Microscope (SEM) analysis (see Figs. 4–8), with the detector components being outlined in Table 2. The model was validated by comparison with the measured calibration curve and agreement achieved to ± 2% (r = 2) or better above 100 keV.
Table 1

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Energy (keV)</th>
<th>Emission probability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{228}$Ra (direct)</td>
<td>186.2 (13)</td>
<td>3.8 (6)</td>
</tr>
<tr>
<td>$^{228}$Ra (via $^{228}$Rn)</td>
<td>265.2 (2)</td>
<td>18.2 (3)</td>
</tr>
<tr>
<td>$^{232}$Th (via $^{228}$Rn)</td>
<td>351.9 (2)</td>
<td>35.1 (3)</td>
</tr>
<tr>
<td>$^{232}$Th (via $^{228}$Ac)</td>
<td>609.3 (7)</td>
<td>44.6 (3)</td>
</tr>
<tr>
<td>$^{232}$Th (via $^{228}$Ac)</td>
<td>1120.3 (10)</td>
<td>14.7 (2)</td>
</tr>
<tr>
<td>$^{232}$Th (via $^{228}$Ac)</td>
<td>1744.5 (14)</td>
<td>15.3 (3)</td>
</tr>
<tr>
<td>$^{235}$U (via $^{227}$Th)</td>
<td>328.5 (2)</td>
<td>11.3 (12)</td>
</tr>
<tr>
<td>$^{237}$U (via $^{227}$Th)</td>
<td>912.4 (4)</td>
<td>29.9 (4)</td>
</tr>
<tr>
<td>$^{230}$Th (via $^{227}$Th)</td>
<td>969.0 (7)</td>
<td>25.8 (3)</td>
</tr>
<tr>
<td>$^{233}$Th (via $^{227}$Th)</td>
<td>228.6 (2)</td>
<td>43.3 (3)</td>
</tr>
<tr>
<td>$^{233}$Th (via $^{227}$Th)</td>
<td>585.2 (2)</td>
<td>30.4 (2)</td>
</tr>
<tr>
<td>$^{233}$Th (via $^{227}$Th)</td>
<td>1436.6 (2)</td>
<td>11.6 (3)</td>
</tr>
<tr>
<td>$^{235}$U (via $^{227}$Th)</td>
<td>205.3 (2)</td>
<td>5.01 (3)</td>
</tr>
<tr>
<td>$^{237}$Np (via $^{235}$U)</td>
<td>766.4 (2)</td>
<td>0.3 (12)</td>
</tr>
<tr>
<td>$^{238}$U (via $^{235}$U)</td>
<td>1004.3 (8)</td>
<td>0.8 (19)</td>
</tr>
</tbody>
</table>

2.4.2. Alpha spectrometry

The sources were prepared by electroplating (Haltradium, 1984) and counted in an ORTEC Octre Plus α-particle spectrometer with Passivated Implanted Planar Silicon (PIPS) detectors and ORTEC Maestro Multichannel Analyzer (MCA) application software. The energy calibration of the detectors was performed with a $^{241}$Am, $^{241}$Cm and $^{237}$Np source. The sources were counted for 300,000 s, as close as possible to the detector, with an estimated counting efficiency of 21% based on the solid angle coverage. The instrument backgrounds were measured prior to the sample measurement.

2.4.3. Inductively coupled plasma mass spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry has been proven as a suitable alternative to radiometric techniques (α and β decay counting techniques) for the determination of a range of long-lived radionuclides such as $^{228}$Th and $^{232}$U (Caruana et al., 2014). Samples were measured using an Agilent 8800 ICP-QQQ MS (Arn et al., 2016). The instrument was fitted with a quartz double-pass spray chamber and a MicroMist nebulizer and nickel sample and skimmer cones. The instrument was operated in single-quadrupole mode throughout, and tuned daily using a mixed 1 µg g$^{-1}$ standard solution, with no additional thorium and uranium-specific tuning carried out. Calibration standards were prepared for $^{227}$Th, $^{228}$Th, $^{228}$U and $^{232}$U to determine instrument performance, limits of detection and to calculate recoveries. The measurement time was approximately 600 s per sample, with the integrated auto-sampler enabling the elution fractions for $^{228}$Th and $^{228}$U in all matrices to be counted within one working day. Instrument backgrounds were counted before and after each sample. The ICP-MS standards used were approximately two orders of magnitude less concentration of the radionuclides of interest than the final analysed samples for $^{227}$Th and $^{228}$U. We estimate that this leads to an uncertainty in the extrapolated conversion between counts per second and activity concentration in the measured a sample region of approximately a factor of 2 for the ICP-MS results in the current work. The absolute activity measurements quoted in Tables 3 and 4 are based therefore on the γ and α spectrometry measurements.

3. Results and discussion

The results for the two main decay series are given in Tables 3 and 4. The radiometric results suggest that the earth is in near-equilibrium for both the 4n and 4n+2 decay series and there is reasonable consistency between the independent α-particle and γ-ray spectrometry measurements. This may be a result of the lack of processing of such material which, as stated above, is used directly as a building material.

Considering the sand, the picture is somewhat different as both the 4n and 4n+2 series are in disequilibrium. Setting aside the ICP-MS data, the material appears to be enclathrated in radium but depleted in thorium. This may be a consequence of the solubility of radium in water across a wide range of pH values, whereas thorium tends to only be soluble in low pH aqueous solvents. Furthermore, it may also be the case that the binding sites on sand preferentially adsorb radium. The activities and uncertainties of the 4n series in sand are such that no firm conclusions can be drawn from this data.

For the thorium dioxide, it is clear that both the 4n and 4n+2 series are in disequilibrium, and it appears to be enriched in radium but depleted in thorium. This may be a consequence of the material processing, which is complex, and was not defined in detail by the supplier. However, it has been observed (Finazzo et al., 2015) that most of the radium remains associated with the un-dissolved material.

<table>
<thead>
<tr>
<th>Element</th>
<th>%α (k=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>44.1 ± 0.9</td>
</tr>
<tr>
<td>Ti</td>
<td>41.7 ± 0.9</td>
</tr>
<tr>
<td>S</td>
<td>9.2 ± 0.4</td>
</tr>
<tr>
<td>Fe</td>
<td>2.8 ± 0.2</td>
</tr>
<tr>
<td>H</td>
<td>2.2 ± 0.1</td>
</tr>
</tbody>
</table>

Fig. 1. GEANT4 model of lanodot (Semi-Planar detector).

Fig. 2. Backscattered electron image of TiO₂ and its detected elemental composition.
waste, with their work measuring radium activity concentrations into the lBq kg⁻¹ levels. The association of radium with undissolved waste is primarily a result of the digestion process of the fissionable material with concentrated sulphuric acid, leading to precipitation of radium as radium sulphate (RaSO₄), the insolvency of which is well known (Landa, 2007).

The results for ²²⁶⁰Ra (t₁/₂ = 1.91 years) and its decay products are rather ambiguous. Although the levels of ²²⁶⁰Ra (t₁/₂ = 5.75 years) and the ²²⁶⁰Ra (t₂/₂ = 3.66 days) sub-series are similar (although the ²²⁶⁰Ra sub-series is depleted with respect to ²²⁶⁰Ra in tuff) the activity concentration of ²²⁶⁰Th determined by α-spectrometry is rather low, from which one might conclude that there has been incomplete dissolution.

For the 4n + 2 series, it is clear that ²²⁸⁰Th (t₁/₂ = 7.54 × 10⁸ years) is depleted with respect to ²²⁴⁰Ra (t₁/₂ = 1.6 × 10⁵ years) even if the 5–6 times lower measurement of ²²⁸⁰Th with α-spectrometry compared to γ-spectrometry is taken into account (see Figs. 5 and 6). This is particularly true for the tuff and one may conclude that radium is more strongly bound than thorium to tuff. However, it is difficult to resolve these observations without further experiments aimed at leaching (rather than dissolving) the various matrices (Coadace et al., 1980).

4. Conclusions

The measurement of NORM radionuclides in the three chosen standard reference materials has been undertaken. The dissolution process may not recover all of the thorium present in the samples and more work may be necessary to determine the levels of thorium isotopes with improved accuracy. The γ-ray spectrometry results are

<table>
<thead>
<tr>
<th>Element</th>
<th>% (k=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>34.4 ± 0.9</td>
</tr>
<tr>
<td>K</td>
<td>19.6 ± 0.8</td>
</tr>
<tr>
<td>Ca</td>
<td>17.6 ± 0.8</td>
</tr>
<tr>
<td>AL</td>
<td>12.3 ± 0.7</td>
</tr>
<tr>
<td>Fe</td>
<td>10.7 ± 0.6</td>
</tr>
<tr>
<td>Ti</td>
<td>1.4 ± 0.2</td>
</tr>
</tbody>
</table>

Table 2: List of additional items. Description of detector components that make up the SWROD model.

<table>
<thead>
<tr>
<th>Item</th>
<th>Material</th>
<th>Model shape</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detector front window</td>
<td>Carbon fibre</td>
<td>Cylinder</td>
<td>3.00 cm height</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.17 cm radius</td>
</tr>
<tr>
<td>Detector outer case</td>
<td>Carbon fibre</td>
<td>Cylinder</td>
<td>3.00 cm height</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.25 cm outer radius</td>
</tr>
<tr>
<td>Detector Geiger tube</td>
<td>Germanium</td>
<td>Cylinder</td>
<td>3.00 cm height</td>
</tr>
<tr>
<td>Detector beam coll.</td>
<td>Germanium</td>
<td>Three stacked</td>
<td>Radius 1: 4.20 cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>truncated cones</td>
<td>Radius 2: 4.85 cm at</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.30 cm high</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.63 cm high</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.92 cm high</td>
</tr>
<tr>
<td>Detector dead layer</td>
<td>Germanium</td>
<td>Part of truncated</td>
<td>2.60 cm height</td>
</tr>
<tr>
<td>Conical wall</td>
<td>Vacuum</td>
<td>cone</td>
<td>3.45 cm radius</td>
</tr>
<tr>
<td>Conical well and</td>
<td>Vacuum</td>
<td>Translated cone</td>
<td>Radius 1: 4.44 cm</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>Copper</td>
<td>Hollow cylinder</td>
<td>4.66 cm height</td>
</tr>
<tr>
<td>Source mount holder</td>
<td>Polystyrene</td>
<td>Hollow cylinder</td>
<td>6.69 cm outer radius</td>
</tr>
<tr>
<td></td>
<td>methacrylate</td>
<td></td>
<td>9.49 cm thickness</td>
</tr>
</tbody>
</table>

Fig. 3. Back-scattered electron image of tuff and its detected elemental composition.

Fig. 4. Back-scattered electron image of rad and its detected elemental composition.
Table 3
Thin film (%e) series results.

<table>
<thead>
<tr>
<th>Nucleide</th>
<th>Technique</th>
<th>Sand (kg/kg) (k = 2)</th>
<th>TiO₂ (kg/kg) (k = 2)</th>
<th>Tuff (kg/kg) (k = 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>²²⁶Ra</td>
<td>α-spectrometry</td>
<td>7 ± 1</td>
<td>16</td>
<td>484</td>
</tr>
<tr>
<td>²³⁹Pu</td>
<td>α-spectrometry</td>
<td>1.3 ± 0.1</td>
<td>9.2 ± 0.4</td>
<td>520 ± 18</td>
</tr>
<tr>
<td>³⁵⁴mSm (via ²⁴⁰Pu)</td>
<td>γ-spectrometry</td>
<td>7 ± 1</td>
<td>21,200 ± 1,400</td>
<td>356 ± 19</td>
</tr>
<tr>
<td>³⁹⁰Th (via ²³⁹Pu)</td>
<td>γ-spectrometry</td>
<td>5.0 ± 0.2</td>
<td>3,450 ± 110</td>
<td>322 ± 18</td>
</tr>
<tr>
<td>³⁹⁰Th (via ³⁹⁰Th)</td>
<td>γ-spectrometry</td>
<td>7.0 ± 0.9</td>
<td>15,600 ± 1,300</td>
<td>354 ± 24</td>
</tr>
<tr>
<td>³⁹⁰Tm</td>
<td>γ-spectrometry</td>
<td>7 ± 1</td>
<td>18,500 ± 260</td>
<td>353 ± 6</td>
</tr>
</tbody>
</table>

Table 4
Uranium (%e + 2) series results.

<table>
<thead>
<tr>
<th>Nucleide</th>
<th>Technique</th>
<th>Sand (kg/kg) (k = 2)</th>
<th>TiO₂ (kg/kg) (k = 2)</th>
<th>Tuff (kg/kg) (k = 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>²³⁸U</td>
<td>α-spectrometry</td>
<td>26 ± 1</td>
<td>13 ± 0.3</td>
<td>309 ± 10</td>
</tr>
<tr>
<td>³⁹⁰Th</td>
<td>α-spectrometry</td>
<td>10 ± 1</td>
<td>13 ± 0.3</td>
<td>309 ± 10</td>
</tr>
<tr>
<td>³⁹⁰Th</td>
<td>γ-spectrometry</td>
<td>&lt; 34</td>
<td>&lt; 31</td>
<td>426 ± 92</td>
</tr>
<tr>
<td>³⁹²Th</td>
<td>α-spectrometry</td>
<td>17 ± 2</td>
<td>15.7 ± 0.5</td>
<td>350 ± 17</td>
</tr>
<tr>
<td>³⁹²Th</td>
<td>γ-spectrometry</td>
<td>11.2 ± 0.4</td>
<td>10.0 ± 0.5</td>
<td>331 ± 13</td>
</tr>
<tr>
<td>³⁹⁰Ir</td>
<td>γ-spectrometry</td>
<td>117 ± 33</td>
<td>28,200 ± 2,000</td>
<td>249 ± 30</td>
</tr>
<tr>
<td>³⁹²Ir (via ³⁹⁰Ir)</td>
<td>γ-spectrometry</td>
<td>85 ± 0</td>
<td>26,600 ± 620</td>
<td>213 ± 7</td>
</tr>
<tr>
<td>³⁹⁰Ta (via ³⁹⁰Ir)</td>
<td>γ-spectrometry</td>
<td>84 ± 3</td>
<td>29,000 ± 2000</td>
<td>198 ± 6</td>
</tr>
</tbody>
</table>

Fig. 6. α-particle spectra of sand, TiO₂, and tuff.

such that they can be used to characterise these three materials making them suitable for use as certified reference standards for future measurement of NORM radionuclides with an uncertainty of < 10%.

Acknowledgements

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References


Progress towards the production of the $^{236}$Np standard sources and competing fission fragment production

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**Highlights**

- The isobaric distribution of fission residues.
- Decay analysis of thirteen isobarically distinct fission residues.
- Stoichiometric abundances were calculated via the determination of absolute activity concentrations.
- This technique was validated by computational modelling of likely sequential decay processes.
- The results were largely in agreement with previously published values for neutron bombardments on $^{235}$U at energies of 14 MeV.

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**ABSTRACT**

The isobaric distribution of fission residues produced following the bombardment of a natural uranium target with a beam of 25 MeV protons has been evaluated. Decay analysis of thirteen isobarically distinct fission residues were carried out using high-resolution γ-spectrometry at the UK National Physical Laboratory. Stoichiometric abundances were calculated via the determination of absolute activity concentrations associated with the longest-lived members of each isobaric chain. This technique was validated by computational modelling of likely sequential decay processes through an isobaric decay chain. The results were largely in agreement with previously published values for neutron bombardments on $^{235}$U at energies of 14 MeV. Higher yields of products with mass number $A \sim 110-130$ were found consistent with the increasing yield of these radionuclides as the bombarding energy is increased.

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1. Introduction

The radionuclide $^{236}$Np is of interest both as a long-lived odd-odd radionuclide and as a chemical yield tracer for the radiochemical analysis of $^{237}$Np (Jerome et al., 2014). Neptunium-237 is significant in a number of fields of research such as nuclear forensics, environmental analysis and the nuclear fuel cycle. However, investigation of $^{237}$Np is complicated by the radiochemical analysis of $^{237}$Np (Jerome et al., 2014). Neptunium-236 is a potential candidate as a neutron yield tracer, as its 1.55(8) $\times 10^{11}$ years radioactive half-life (Chechlev and Kuzmenko, 2007) allows it to be used for both radiometric and mass spectrometric measurements. One method of $^{236}$Np synthesis that has shown promising results is to bombard $^{238}$U with protons (Jerome et al., 2014). This production method yields a variety of other radionuclides as a result of the high-energy proton-induced fission of $^{238}$U; however there is a scarcity of information regarding the fission yields produced by proton bombardments of this energy on natural uranium targets. In the current work, we present the mass distribution of the fission fragment residues produced following the proton irradiation of natural uranium which were formed in parallel with the production of $^{236}$Np.

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2. Materials and methods

2.1. Target irradiation and sample preparation

A target containing 1 g of uranyl nitrate was produced by compacting $^{238}$U at 60 kN cm$^{-2}$ between an aluminium target holder and a 0.025 mm titanium foil. The target was irradiated at the University of Birmingham UK cyclotron for a total duration of 18.75 h over a period of 3 days (9–11 December 2013), with an incident proton energy of 25 MeV, using an average on-target beam current of approximately 20 $\mu$A. Directly following the irradiation, the target was left for approximately 20 days, thereby allowing the short-lived fission products and their decay daughter residues (i.e., those with $T_{1/2} < 2$ days) to reduce significantly their specific activities. The radiochemical processing of the target was carried out at NPL with the irradiated target of $^{238}$UCl$_3$ · 6H$_2$O being dissolved in nitric acid and converted to an 8 M nitric acid solution. A 1 g aliquot of the solution was then dispensed to a 2 mL glass British standard (BS7995:1983) ampoule for measurement by $\gamma$-spectrometry.

2.2. Gamma spectrometry

The LN$_2$ cooled high purity germanium (HPGe) $\gamma$- spectrometer BART was used to perform a series of measurements of the prepared sample. The details of the detector specifications and the full-energy peak efficiency calibration have been previously described in Collins et al. (2014). The sample was measured twelve separate times for a typical counting time of 50,000 s over the course of several months. The net peak areas of the discrete $\gamma$-emissions associated with specific fission fragment decays were calculated using the Canberra Genie 2000 v2.1c software. The fitted photopeaks were reviewed with the Interactive Peak Fit tool and adjusted where required. The photopeak net peak areas were corrected for background, integrated radioactive decay, and pulse pile-up. No corrections were applied for true coincidence summing as the samples were measured at a source-to-detector window distance of 30 cm (solid angle = 0.45 sr), reducing any coincidence summing to a level which was insignificant compared to the other sources of measurement uncertainty.

2.3. Use of the Bateman equations for elemental activity distribution simulations

The determination of the abundances of each isobaric chain produced by the proton-induced fission of $^{238}$U is complicated by the initial population of a range of elements for each isobaric chain in the fission process. The neutron-rich radionuclides produced directly following the fission events typically have radioactive half-lives in the range of seconds to hours; this means that such radionuclides have undergone sufficient radioactive decays to bring their abundances below the minimum detectable activity by the time of the initial $\gamma$-spectrometry measurement in the current work. The decay of fission products through their respective mass chains towards stability is generally accompanied by increasing half-lives as the line of stability is approached. Many of the isobaric decay chains from $A \approx 80$ to $\approx 160$ decay through well-defined radionuclide species with characteristic $\gamma$-emissions following their decay by $\beta$-emission to excited states in the final, long-lived daughter nucleus of that particular mass chain. These penultimate members of the isobaric fission fragment decay chains can have sufficiently long half-lives (days to months) to be a useful monitor of the decay activity in the present work.

The total number of atoms produced in a given mass chain can be estimated without prior knowledge of the initial elemental ($Z$) distribution of the members within that mass chain following the initial fission using the assumption that the decay lifetime of the ultimate decay in the chain is significantly longer than each preceding decay half-life.

The basis of any such solution of a decaying nuclear chain must take into account the Bateman equations of radioactive decay (Bateman, 1910) for that chain. The number of atoms of the first radionuclide ($N_1$) within the series is given by the normal exponential decay equation:

$$N_1(t) = N_1(0)e^{-\lambda t}$$  \hspace{1cm} (1)

where $N_1(t)$ is the number of atoms at time $t$, $N_1(0)$ is the initial number of atoms when $t = 0$ and $\lambda$ is the decay constant. To model the system, the number of atoms present and their rate of change with respect to time (i.e., the activity) needs to be calculated.

Under the assumption that the parent radionuclide in the chain has a fixed amount of atoms, $N_1(0)$ at the effective time zero ($t = 0$) and no further production of the parent radionuclide takes place, then the activity associated with this radionuclide is given by

$$\frac{dN_1}{dt} = \frac{d}{dt}N_1(0)e^{-\lambda t} = -\lambda N_1(0)e^{-\lambda t} = -\lambda N_1(t)$$  \hspace{1cm} (2)

If $N_1$ decays exclusively to a daughter radionuclide ($N_2$) then the rate of change of number of atoms of $N_1$ is given by

$$\frac{dN_1}{dt} = \lambda_1 N_1 - \lambda_2 N_2$$  \hspace{1cm} (3)

Similar arguments hold for the following nuclei up to and including the terminal radionuclide ($N_n$);

$$\frac{dN_n}{dt} = \lambda_n N_{n-1} - \lambda_n N_n$$  \hspace{1cm} (4)

If the nth member of the decay chain represents a radioactively stable species (i.e., $\lambda_n N_n = 0$), then $\frac{dN_n}{dt} = \lambda_n N_{n-1}$.

A decay simulation was produced based on the matrix based algebraic approach to the Bateman equations given by Moral and Pacheco (2003), detector efficiency and $\gamma$-emission probability so that the effect of varying the initial distribution of radionuclides on the strength of the $\gamma$-emissions could be measured. It was established that the activity of the longest-lived member in a chain could be related directly to the initial number of atoms at the effective zero time of the irradiation, provided the previous members in the chain were short-lived by comparison. This is indeed the case for most isobaric decay chains between $A \approx 80$–160 due to the time it takes for the more neutron-rich, shorter-lived ($T_{1/2} \approx$ seconds to minutes) members of a particular mass chain to decay through to the longest-lived member being negligible with respect to the half-life of the long-lived member, i.e., that closest to stability which can have $T_{1/2} \approx$ days to months. This approximation overestimates the initial number of atoms by an amount dependent on the initial distribution of the atoms within a particular mass chain. The largest overestimation occurs when the initial atoms in the mass chain are all formed in the chain member with the highest neutron-to-proton ratio (i.e., most neutron-rich). The majority of the mass chains were found to have maximum overestimations of 0.1%. Since the initial elemental distribution was not established, the current work makes the gross assumption of a 'rectangular distribution' of the initial elemental population (i.e., an equal elemental production for all isobaric chains of neutron-rich nuclei that there is half-life data for). This was fed into the computational calculation and the overestimation (or underestimation) used to calculate the correction factor to be applied to the measurements. For example, in the case of $^{92}$Zr the initial ratio of $^{92}$Kr to $^{92}$Zr was assumed to be 1:1:1:1:1:1 and the decay of this system then modelled. This was used to calculate a
likely correction factor (between $^{95}$Zr measurements and $N_0$). The simulation was then run again with the ratio as 1:0:0:0:0, giving a maximum overestimation. The effective uncertainty in the simulated values arising from the correction factor was estimated to be $1/[2\sqrt{3}]=0.29$ multiplied by the maximum overestimation from the true value (this in accordance with a one-standard deviation value for a rectangular distribution). Fig. 1 shows the results of a simulation for the maximum overestimation of $^{95}$Zr as an example. Note that a projection back to $t_0$ on the number of atoms of $^{95}$Z as at the end of the simulation gives good agreement with the actual value of $N_0$ used.

2.4. Evaluation of successive isobaric decays and extrapolation to an effective zero-time production

The $\gamma$-spectra of the fission products sample (an example is given in Fig. 2) were analysed to identify the radionuclides present, with particular emphasis being given to decays identified from neutron-rich radionuclides with mass numbers between $A=70$ and 170 (fission fragments). The corrected activity associated with these specific $\gamma$-emissions were plotted as a function of time. The slopes of these individual decay curves were fitted to single-component exponential decay functions to check the radioactive decay half-life was consistent with the evaluated value for that particular radionuclide. If there was not agreement with published half-lives, other possible sources which could be causing interference were considered and systematically removed until the $\gamma$-emissions were all assigned. As an example, the

![Fig. 2. Gamma spectrum of identified radionuclides from the bombardment of $^{95}$U by 25 MeV protons approximately two months after the irradiation period.](image)

![Fig. 3. A plot of yield vs. atomic weight of mass chains for the induced fission of natural uranium. The data points represent the values found during this experiment (irradiation with 25 MeV protons) whilst the dashed line represents the data for 14 MeV neutrons as derived from Vallet et al. (2009). The uncertainties on this data represent an uncertainty of one standard uncertainty. Error bars are at 1 S.D.](image)

1088 keV line was identified as indicating the presence of $^{123}$Sn, $^{96}$Co or $^{123}$Sn, however the half-life was not in agreement with any of their published values. After determining the activities of $^{96}$Co and $^{123}$Sn from their other gamma emissions however, their contributions to the 1088 keV peak could be subtracted, leaving a peak with the correct half-life for $^{123}$Sn.

The activity of the radionuclide at the effective zero time was the calculated independently for each contributing $\gamma$-emission from each spectrum and the results compared the effective zero-time was calculated using the $^{95}$Zr-$^{239}$Nd chronometry method detailed by Pomme and Collins (2014). If the lines converged to
approximately the same activity (when uncertainties in γ-emission probabilities, detector efficiency and counting statistics were considered) and all of the above tests were passed then the γ-emission was considered to have no further unseen interferences present.

The activity at $t_0$ was calculated as the weighted mean of the determined activities for each γ-emission for a given radionuclide.

The calculated activity of a radionuclide at the effective time zero ($A_{0}$) was then converted to the initial number of atoms ($N_{0}$) produced for a particular isobaric chain using the simple relation:

$$N_{0} = \frac{A_{0}}{\lambda}$$

(5)

where $A_{0}$ is the effective time zero activity in Bq and $\lambda$ is the decay constant of the longest-lived member of the isobaric decay chain. The value was corrected for potential overestimation utilising the correction factor calculated from the Bateman simulations described in Section 2.3. The final standard uncertainty was calculated as the quadratic sum of the theoretical uncertainty from the Bateman simulations and the weighted experimental uncertainty calculated in this section (combining spread in the data, counting statistics, full-energy peak efficiency and published emission probabilities).

3. Results

Of the radionuclides identified, those corresponding to fission fragments and their daughters’ decays were selected for further analysis. Specifically, only those nuclides which were not preceded in their decay chains by longer-lived nuclides were considered. These were converted to a fission yield (expressed as a percentage) and scaled so that the $^{95}Zr$ yield was in agreement with the published value for 14 MeV neutron bombarding ($Kellett et al., 2009$) when the total published yields are standardised to add to 100% (as each fission event would result in two residual nuclei). This point was chosen for standardising as the $^{95}Zr$ value had the lowest uncertainty. Fig. 3 shows these data points from the current work along with that from Kellett et al. (2009), database values for the fission mass distribution expected from 14 MeV neutrons on $^{238}U$ as a comparison (Table 1).

The experimental data points on the two mass abundance peak regions at A = 95 and A = 140 are in good agreement with the published values based on 14 MeV neutron irradiations. There are however some noticeable differences with the trough between the two peaks corresponding to near-symmetric fission (i.e. the data for mass chains between A = 110 and 130) being less prominent for the proton-induced data from the current work, indicating higher yields of these nuclides in this bombardment. In addition, the data for $^{152}Eu$ also indicates a higher yield of this mass chain than was found in Ref. Kellett et al. (2009) evaluation.

It has been found in the nuclear data database JEFF 3.1 that, for neutron induced fission, the shape of the yield distribution changes in a predictable way as the energy of the incident neutrons is varied. Specifically, the relative fission yields for near symmetric fission (mass chains 110–130) increase and the gradient of the fission yield curve adjacent to this mass region decreases as
the neutron energy increases. This corresponds to an increase in the fission yields of mass chains that are not on the peaks. As the energy of the protons is almost double that of the closest available neutron irradiation data, it is likely that the differences are due to this increased energy rather than a major difference between proton and neutron irradiations. This is further supported by the good agreement between the experimental and published data for the points located around the peaks, which do not change with energy. The lower than predicted yield observed for the A=131 chain (which was evaluated using decay of $^{127}$I) may arise due to the volatile chemical nature of iodine and the possible related loss of material during the chemical processing of the target.

4. Conclusions

The results obtained from this study of fission products derived from the proton irradiation of natural uranium has shown that the yield distribution plot obtained is in good agreement with the referenced value obtained from the neutron induced fission with 14 MeV neutrons as published in Kollet et al. (2009). The shape of the yield distribution displays variations consistent with the trend of increasing energy seen as incident neutron energy is varied.

Acknowledgments

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References

The production of Neptunium-236g

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ABSTRACT

Radiochemical analysis of 236gNp is important in a number of fields, such as nuclear forensics, environmental analysis and measurements throughout the nuclear fuel cycle. However analysis is complicated by the lack of a stable isotope of neptunium. Although various tracers have been used, including 235gNp, 237gNp and even 239gPu, none are entirely satisfactory. However, 236gNp would be a better candidate for a neptunium yield tracer, as its long half-life means that it is usable as both a radiometric and mass spectrometric measurement. This radiotracer is notoriously difficult to prepare, and limited in scope. In this paper, we examine the options for the production of 236gNp based on work carried out at NPL since 2011. However, this work was primarily aimed at the production of 235gNp, and not 236gNp and therefore the rate of production are based on the levels of 239gPu generated in the irradiation of (γ, n)238U with protons, (3He, n)233U with deuterons, (8Li, n)239U with protons and (4He, t)235U with deuterons. The derivation of a well-defined cross section is complicated by the relevant paucity of information on the variation of the 236gNp yield with incident particle energy. Furthermore, information on the purity of 236gNp so produced is similarly sparse. Accordingly, the existing data is assessed and a plan for future work is presented.

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1. Introduction

1.1. Chemical yield tracers

In selecting an isotope dilution tracer a number of requirements should be met (Harvey and Lovett, 1984):

- The tracer must exhibit the same chemical behaviour as the analyte, and thus the tracer should be the same element as the analyte.
- The tracer should not interfere with the measurement of the analyte and it is thus preferable to measure both the analyte and tracer by the same technique, or that the tracer does not register in the analyte measurement (and vice versa), and
- That chemical equilibrium between the tracer and analyte should be established at the earliest possible point in the analysis. This requires that the tracer should be added as soon as possible in the analysis and (for solids) employ total dissolution.

Furthermore, one should also consider that:

- The tracer should not be initially present in the samples being analysed, since using nuclides present in the samples being analysed complicates analysis,
- The tracer should be pure and not introduce contamination into samples being measured, especially the analyte. This puts a stringent purity requirement on the tracer that may differ for mass spectrometry and radiometric measurements, and
- The tracer activity should be traceable to national or international standards, although this may not be necessary where the yield can be determined by comparative measurements, such as γ emitting tracers.

This constrains the choices available for a suitable neptunium tracer. Bearing in mind the difficulty of obtaining a neptunium chemical yield tracer and the data quality requirements for such measurements, it may be possible to employ a plutonium yield tracer, such as 239Pu (for example: Maxwell et al., 2011; Thakur and Muhlolland, 2012). This approach is indeed acceptable (and has been very successful) for measurements where a higher level of uncertainty may be tolerated. However, there is always the risk of speciation of neptunium and plutonium during analysis and this
may be especially so in solid matrices. For high precision work, including measurements for forensic purposes, it is essential that the tracer is a neptunium isotope. There are a number of neptunium isotopes that could potentially be employed, and these are set out in Table 1 (Durley, 1987; ENSDF). The practical candidate neptunium isotopes are $^{235}$Np, $^{236}$Np and $^{237}$Np, of which only $^{238}$Np is really suitable for mass spectrometry. $^{237}$Np has an activity of ~52 kBq/µg. Neptunium-236g has been produced intermittently, although much of it as a by-product of the production of $^{238}$Pu (Furth et al., 1981). Since 2005, as part of NPL’s work to maintain regular supplies of $^{238}$Pu, irradiation of various uranium isotopes has been carried out at the University of Birmingham, with chemical separation and measurement work carried out at NPL.

1.2. The low-lying structure of the odd–odd nucleus $^{236}$Np

The spin and parity of low-lying states in odd–odd nuclei (i.e., radioisotopes with a single unpaired neutron and proton in the outer orbit) are determined by the vector, axial, magnetic and electric nematic coupling of the two unpaired particles (Gallagher and Moszynski, 1958).

The radioisotope $^{236}$Np is of interest both as a long-lived odd–odd isotope and as a chemical yield tracer. The parallel and anti-parallel couplings of the final unpaired proton and neutron in this nucleus gives rise to two competing states with the same internal, single-particle configuration, which have assigned spin-parity $I^+ = (6−)$ and $(1−)$ respectively. The higher-spin, high-K coupling has been established as the ground state of this proton deformed nucleus and decays with a half-life of 1.53 × 10^5 years. The anti-parallel coupling of the Nilsson orbitals gives rise to the meta-stable, but considerably shorter-lived $I^+ = (1−)$ state, which has an evaluated decay half-life of 22.5 h. Both of these states decay to excited states in $^{238}$U (by electron capture) and $^{238}$Pu (by β^- decay). The spin-parity of the decaying state has been established by the identification of electromagnetic transitions from high spin $(I^+ = 6−)$ and low-spin $(I^+ = 2−)$ states respectively which are populated in the daughter nuclei. The excitation energy difference between the $I^+ = 6−$ ground state and $I^+ = 1−$ excited state has not been experimentally established to date but evaluations suggest an energy difference of the order of 60 eV. This energy difference would give a direct measurement of the Nilsson orbital dependent proton-neutron resonant and neutron in this nucleus.

Table 1

<table>
<thead>
<tr>
<th>Nucleide</th>
<th>Half-life</th>
<th>Production route</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{235}$Np</td>
<td>4.4 days</td>
<td>$^{235}$U(p,n) or (d,ln)</td>
<td>Unlikely to be able to produce by this route, due to scarcity of suitable pure target material.</td>
</tr>
</tbody>
</table>
| $^{234}$U(p,2n) or (d,ln) | | Separation of $^{235}$Np needed to carry out.
| $^{235}$U(p,n) or (d,ln) | | "out relatively quickly, in the presence of large amounts of fusion products."
| $^{237}$Np | 390.3 days | $^{237}$U(n,2n) or (d,ln) | Unlikely to be able to produce by this route, due to scarcity of suitable pure target material. |
| $^{236}$U(n,2n) or (d,ln) | | "Produced in some of these runs, although the irradiation conditions of $^{237}$U (e.g., $^{237}$U) are preferred as this avoids the formation of $^{237}$Np. The decay mode of $^{237}$Np (45% $^{237}$P)
| $^{238}$U | 2.25 h | $^{238}$U(n,2n) or (d,ln) | The short half-life of this nuclide is too short to be practical. It is, however, a route to the production of $^{238}$Pu. |
| $^{239}$Np | 3.5 × 10^5 years | $^{239}$U(n,2n) or (d,ln) | The half-life and decay mode of $^{239}$U of this isotope make it suitable for mass spectrometry or radiometric determination. |
| $^{237}$U | | | The ratio of formation of $^{237}$Np is not well defined. |
| $^{236}$Np | | | Production by three routes are worth noting, without subsequent isotope separation. |
| $^{234}$Am | 2.102 days | $^{234}$U(p,n) or (d,ln) | It is possible to use $^{234}$Np as a yield tracer (β^- emitting) in some short half-life and especially the production route makes it impractical. Similar comments to $^{236}$Np apply, although the alternative production route via decay of $^{234}$Am makes this more attractive and this isotope is commonly used as a yield tracer. |
| $^{234}$Am | 2.358 days | $^{234}$U(p,2n) or (d,ln) | |
0+ ground states and first 1+ - 2+ states in the 239Pu and 239Pu daughter nuclei, with a weak direct decay branch also identified the K0 - 2 excited state at 687.7 keV in 239Pu (Lederer et al., 1969). The electromagnetic (M) direct decay branch from the 238Np (1') metastable state to the proposed K0 - 6' - 1260Np ground state has not been identified experimentally to date.

2. Neptunium-238g

Neptunium-238g is always accompanied by 239Np, when produced and the production ratio between 238Np and 239Np is dependent on incoming particle energy, with low ratios (leaving 238Np production) being favoured by higher incident particle energy (Aaltoenen et al., 1990). This is associated with the input angular momentum of the production reaction used for the production of 238Np. For production using the 239Pu(p,n)238Np reaction, the increase in production ratios between the 238Np and 239Np is shown to increase systematically with increasing input angular momentum and thus beam energy (see Fig. 5 in Aaltoenen et al., 1990), with a ratio of close to unity estimated for input angular momenta of ~15 h.

The decay of 238Np generates a number of B-particles and y-rays (Chechun and Kurnosov, 2005) and are detailed in Table 2. The states populated following the decay of 238Np are shown in Fig. 1.

3. Neptunium-238g production

The irradiation of uranium with charged particles has been studied by a number of groups around the world, including USA, UK, Finland, Russia and Japan. These groups have generated data about cross sections, although when the results are compared, there do appear to be a number of inconsistencies. Since natural uranium, high enrichment 235U and high enrichment 238U are the only target materials available to NPL, only proton and deuterium irradiation of these isotopes will be considered further. The possible routes to production are set out in Table 3.

3.1. Uranium-238

Several groups have irradiated 238U with protons (Aaltoenen et al., 1990, 1994; Agren et al., 1987; Bellido et al., 1994; Gzowsiak et al., 1994; Zhao et al., 1999), but none provide experimental data concerning the formation of 237Np, although Bellido et al. (1994) carry out an estimation of this cross section, based on an optical model, predicting that the cross section for 237Np formation peaks at around 12–15 MeV for protons. The published data is summarised in Fig. 2 and shows some consistency between the various data sets. There is some data to suggest that 237Np is formed by the (p,2n) reaction, although the cross sections are <10^-6 b (Migneco et al., 1977). We can note from this plot that the optimum energy window for 237Np formation is ~15–30 MeV, while that for 235Np is ~25–40 MeV.

When considering deuterium irradiation of 238U (Bellido et al., 1993; Gzowsiak et al., 1994; Leslau et al., 1960; Wing et al., 1960),

Table 2

<table>
<thead>
<tr>
<th>238Np decay data (Chechun and Kurnosov, 2005)</th>
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</thead>
<tbody>
<tr>
<td>Decay transitions</td>
</tr>
<tr>
<td>β</td>
</tr>
<tr>
<td>Electron capture</td>
</tr>
<tr>
<td>y</td>
</tr>
<tr>
<td>45.244</td>
</tr>
<tr>
<td>95.6</td>
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<td>102.02</td>
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</tr>
<tr>
<td>109.361</td>
</tr>
<tr>
<td>142.437</td>
</tr>
<tr>
<td>142.547</td>
</tr>
<tr>
<td>167.58</td>
</tr>
</tbody>
</table>

Fig. 1. Neptunium-238g decay scheme.

Fig. 2. Activation cross sections for 239Pu(p,n)238Np.
a similar picture emerges, although there appears to be a sharper peak in the $^{237}$Np formation cross section, and the energy window for the $^{237}$Np formation is increased by $\approx 5$ MeV, when compared with proton irradiation. There are some discrepancies in published data summarised in Fig. 3.

The excitation energy study by Aaltimate et al. (1990) using the $^{237}$Np(,$d$,n)$^{238}$Np fusion–evaporation reaction shows the maximum production cross-section for both the long-lived ($I_f = 6^+_1$) and short-lived ($I_f = 1^+_1$) decaying states in $^{238}$Np maximise at a beam energy of approximately 21 MeV. The ratio of high-spin ($^{238}$Np) to low-spin ($^{237}$Np) production was found to increase with increasing beam energy, with the production of $^{238}$Np levelling out at constant value of approximately 10 mb for beam energies between 20 and 28 MeV. The measured production cross-section for the shorter-lived $I_f = 1^+_1$ isomeric state drops by a factor of approximately three over the same beam energy range.

The increased input angular momentum associated with the $^{237}$U(d,n)$^{238}$Np reaction (see Bellido et al. 1993) compared to the proton induced reaction may be of specific interest. The peak production cross-section for the deuteron-induced reaction is reported to be approximately 60 mb at a beam energy of 27 MeV, suggesting that this may be the most favourable reaction for the production of a $I_f = (6^+_1)$ $^{238}$Np tracer.

Again, there is no information to describe the formation of $^{238}$Np, although it is reasonable to suppose that it lies at around 15–20 MeV.

### 3.2. Uranium-236

The irradiation of $^{238}$U ($t_1/2 = 23.43(6) \times 10^6$ years, DDPA) is compromised by the availability of the nucleus in a sufficiently pure state. However, production results have been obtained for proton irradiation (Aaltome et al. 1996, 2005) and the published data is shown in Fig. 4.

There are some similarities between this data and that for $^{238}$U in that the cross sections for the (p,n) reaction is $\sim 10–15$ mb. Although the (p,n) reaction is not considered in this paper, the maximum of the cross section is at $\sim 25$ MeV which is similar to the same reaction on $^{238}$U.

When this is compared with the deuteron irradiation of $^{238}$U (Lessler et al. 1996), shown in Fig. 5, the maximum for formation of $^{238}$Np is shifted by $\sim 5$ MeV compared with proton irradiation.

The energy window for the formation of $^{238}$Np is $\sim 10–25$ MeV and that for $^{238}$U is $\sim 15–25$ MeV. This suggests that the $^{238}$U(d,n) reaction forming $^{238}$Np in the deuterium irradiation of $^{237}$U occurs in the same energy region as predicted by Bellido et al. (1993).

### 3.3. Uranium-235

The authors are not aware of any reported data for proton irradiation of $^{235}$U (apart from fission) and the deuteron data (Bellido et al. 1993; Lessler et al. 1966; Wing et al. 1959) is somewhat inconsistent, as shown in Fig. 6. It can be seen that there
is a peak at $\sim 15$ MeV for the $(d,2n)$ reaction cross section and that the $(d,n)$ cross section is approximately constant between 5 and 10 MeV. Efurd et al. (1991) reported the formation of $^{268}$Np in their irradiation of $^{235}$U. It is assumed that the thickness of their target ($\sim 1.3$ g/cm$^2$) sufficiently reduced the deuterium beam energy to allow the $^{235}$U$(d,2n)^{233}$Np radiative capture reaction to take place.

4. Summary of data

We can draw some preliminary conclusions about the possible optimum routes for $^{238}$U production at this point.

- The published cross sections fall into two groups: (i) higher yield, i.e., $>20$ mb for $^{234}$U$(p,2n)$, $^{234}$U$(d,4n)$ and $^{234}$U$(d,2e)$, and (ii) lower yield, i.e., $<10$ mb for $^{238}$U$(p,n)$ and $^{238}$U$(d,n)$.

- The production of $^{238}$Np is unknown, but by analogy we may conclude that this is: (i) higher yield for irradiation of $^{239}$U with deuterons and $^{239}$U with protons and deuterons, and (ii) lower yield for irradiation of $^{235}$U with deuterons and $^{235}$U with protons, providing the target thickness is controlled.

- Use of higher yield routes is dependent on knowing the formation cross section, in particular with particle energy of $^{237}$Np in each case; this is liable to be challenging. The maximum cross section is predicted (from theoretical considerations) to be at $\sim 15$ MeV for $^{234}$U$(p,2n)$, $\sim 20$ MeV for $^{235}$U$(d,3n)$ and between 10 and 30 MeV for $^{235}$U$(d,n)$, although no published data could be located to support this prediction.

- The favoured production routes for $^{238}$Np are thus likely to be the $^{235}$U$(p,2n)$ and $^{235}$U$(d,4n)$ fusion evaporation reactions, with the higher angular momentum input associated with the deuterons indicating reaction likely to give the smallest isotopic ratio (i.e., relative production of the $\frac{1}{2}^+ - \frac{1}{2}^+$ excited state $^{238}$Np relative to the ground state $^{239}$Np).

- Several groups have irradiated $^{238}$U with protons and successfully produced some $^{238}$Np.

As noted above the initial reason for charged particle irradiation of uranium isotopes was the production of $^{236}$Pu in a suitable pure state for use as a chemical yield tracer in plutonium analysis. Since 2009, these irradiations have been carried out yearly for this purpose.

5. NPI irradiations specifically aimed at production of $^{238}$Np

As noted above, much of the work carried out to date at NPI has been concerned with the production of $^{239}$Pu. However, since 2011 we have actively pursued the production of $^{238}$Np. We have, therefore, assessed material produced in earlier irradiations, as well as from more recent irradiations in order to assess the production rate and radionuclide purity in order to plan future irradiations with the goal of producing at least 1 µg ($\sim 360$ Bq) of $^{238}$Np to be used.

- standardise this radionuclide by either $\beta^{-}, \gamma$ or $\gamma-X$-ray coincidence counting, and
- to prepare standardised material, suitable as an isotope dilution tracer for the mass spectrometric determination of $^{237}$Np.

As noted above, there have been a number of irradiations carried out with different goals. These can be grouped as follows:

- Irradiation of $^{238}$U with either protons or deuterons: There is no requirement to recover the target material from the irradiated target.
- Irradiation of $^{238}$U: The target was 99.89% enriched, so the target material was recovered.
- Irradiation of $^{239}$U: The target was 99.74% enriched, so the target material was recovered.

5.1. Processing of $^{238}$U targets irradiated with protons

The targets – either metallic uranium or $U_2O_3$ – were prepared by compaction into copper or aluminium substrates, with a thin aluminium cover foil. Metallic uranium was only used once, as it rapidly oxidised when irradiated. In either case, the proton irradiated targets were dissolved in nitric acid and converted into an 8M nitric acid solution. This solution was passed through two anion exchange resin (Bio-Rad AG1-X8, 100–200 mesh) columns to adsorb any uranium, neptunium and plutonium. Fission products tend not to adsorb on anion resin under these conditions, so the column was thoroughly washed with further 8M nitric acid to remove fission products (Harvey and Thornton, 1988). Plutonium was removed from the column with 12 M hydrochloric acid that was also 0.1 M with respect to ammonium iodide (Harvey and Thornton, 1988), and the column thoroughly washed with additional 12 M hydrochloric acid to remove residual iodide ion. Neptunium was removed with 4 M hydrobromic acid (Marsh et al., 1978) and reserved for measurement. Residual uranium was removed from the column with 0.1 M hydrochloric acid. It was found that the activation of the copper target substrate produced unacceptable levels of $^{198}$Zn ($\sim 250$ MBq), and so the use of this material was rejected in future work.

Another uranium target was prepared using $\sim 1.1$ g of $U_3O_8(NO_3)_{2-3}$, compacted at 60 kN/cm$^2$ between an aluminium target holder and a 0.025 mm titanium foil. The target was irradiated for 1 h with 22 MeV protons, cooled for 20 days to decrease the activity of short-lived fission products and then processed in the same way.

5.2. Processing of $^{239}$U targets irradiated with deuterons

The targets were prepared by compaction of an evaporated solution of $uranil$ nitrate into an aluminium target substrate, with a thin aluminium cover foil. The deuteron irradiated targets (Efurd
et al., 1991) were dissolved in nitric acid and the resulting solution made alkaline with concentrated ammonia solution to remove 99Mo, 99mTc and 137Cs. The ammonium diuranate precipitate was redissolved in 10 M hydrochloric acid. This solution was passed through two anion exchange resin (Bio-Rad AG1-X8, 100–200 mesh) columns to adsorb any uranium, neptunium and plutonium. Most fission products tend not to adsorb on anion resin under these conditions, but 97Zr and 99Nb are retained. The column was thoroughly washed with further 9 M hydrochloric acid to remove residual fission products. The 99Zr was washed from the column with 6 M hydrochloric acid, but it was noticed that 238U was not removed. Plutonium was removed from the column with 12 M hydrochloric acid that was also 0.1 M with respect to ammonium iodide, and the column thoroughly washed with additional 12 M hydrochloric acid to remove residual iodide ion. Neptunium was removed with ~4.5 M hydrochloric acid (Harvey and Thorsten, 1998) and reserved for measurement. Uranium was removed from the column with 0.1 M hydrochloric acid and retained for repurification and reuse.

5.3. Processing of 239Pu targets irradiated with protons

The targets were prepared by compaction of uranium oxide (a mixture of UO2 and UC6H6 nitrate into an aluminum substrate, with a thin titanium cover foil. The proton irradiated targets were dissolved in 5 ml. 3 M nitric acid, containing 0.1 M NaNO3 and 0.1 M H2O2 as these reduct agent are very efficient in adjusting the oxidation state of neptunium to +IV (Bergenstern et al., 2002). The 239Pu radiochemical recovery was assessed by adding of 1 kBq 239Np, separated from an 140La source. Neptunium-239g as Np(IV) was then separated from the target matrix, 239Pu(VI) and the fission products by extraction chromatography using a TEVA column. The distribution coefficient (Kd) of Np(VI) on TEVA resin from 3 M nitric acid is 5 × 105, while for U(VI) Kd < 10 and the majority of fission products are not well retained (Horwitz et al., 1993). An additional advantage of using TEVA for the separation of neptunium from the target material is the fact that uranium shows less tailing on TEVA resin than conventional ion-exchange resin (Thakur and Mulholland, 2012). The sample was loaded onto a TEVA column, preconditioned with 3 M nitric acid, sequentially rinsed with 30 ml of 3 M nitric acid to remove uranium, lanthanides and other fission products as shown in Fig. 7. Neptunium was finally eluted with 0.5 M hydrochloric acid (Kim et al., 2004).

A second purification step was performed with a single AG1 ion-exchange column by the adsorption of the Np(IV) complex Nd(NO3)3 on the resin from 8 M nitric acid in the presence of 0.1 M sodium nitrite and recovering neptunium by elution with 0.3 M nitric acid (Thakur and Mulholland, 2012). One kBq of 239Np as well as 1 Bq of 238Pu were added prior to separation in order to assess the radiochemical recovery of neptunium and plutonium. Plutonium was reduced to the trivalent state with 9 M hydrochloric acid/0.1 M ammonium iodide and eluted as Pu(III) which has negligible adsorption on the anion exchanger as well as TEVA resin, as a result it is easily eluted (Horwitz et al., 1995). This separation step is shown in Fig. 7.

6. Results to date

6.1. Results from 239U targets irradiated with protons

After the short lived fission products were allowed to decay, the target material was dissolved in 20 ml 5.3 M nitric acid. Then four extraction steps with 30% (v/v) tributyl phosphate in n-dodecane were then carried out in order to remove the target uranium. The resulting solution was further processed by ion-exchange chromatography as shown in Fig. 8.

Fig. 2. Chemical separation of neptunium from irradiated 239U targets, based on extraction chromatography.

The neptunium and plutonium fractions were assayed by γ- and α-spectrometry. The neptunium fraction was dispensed into a 10 ml ampoule and counted for 100,000 s on a well germanium detector. The spectrum in Fig. 9 shows the 160.3 keV line associated with the decay of 239Np. From the spectrum analysis it can be estimated that 30 Bq was 239Np present. The α-spectrometry results showed ~3 kBq 239Pu (t1/2.2.858(8) years (ENSDF)) that was produced from decay of 239Np as well as 238Pu with an activity of 37 Bq. The spectrum also shows the decay of the 232U daughter of 238Pu and from the 232U decay branch.

6.2. Results from 235U targets irradiated with deuterons

These results were generated early on in this project, and were aimed at the production of 233Pu. 235Pu was not directly measured. The irradiation was for ~40 h at a beam current of 30–35 μA. The
fraction was electroplated (Kresin, 1977) and measured by a spectrometer. The spectrum is presented in Fig. 10 and the analysis shows that 2.1 kg of 239Pu were produced. The α-decaying ground state of 239Pu would also be formed in this material via the 238Pu decay of the low-spin, 2− → 1− 238Np [see Ardisson et al., 1994].

7. Conclusions

This work has shown that 239Np can be prepared in a number of different ways. The preferred route in terms of purity and quantity is either the proton irradiation of 238U or the deuteron irradiation of 238U. Of these routes, the irradiation of 239U by protons or deuterons may be preferred due to the ease of procurement of 239U in suitable quantities and the lower neutron production rate (and also fission product generation) of this irradiation.

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References


Preparation of proton rich radionuclides in support of radiochemical analysis

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ABSTRACT
The production of proton rich radionuclides supports a wide range of radiochemical analyses via radioactive yield tracers (\(^{99m}\)Tc and \(^{239}\)Pu). In recent years, NPL and the University of Birmingham cyclotrons have collaborated to produce these, and other, radionuclides.

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1. Introduction

Radiochemical analysis for both technetium and plutonium require the use of radioactive chemical yield tracers, since both elements lack stable isotopes. However, the use of chemical yield tracers is constrained by these limitations (Harvey and Lovett, 1984):

- The tracer must exhibit the same chemical behaviour as the analyte.
- The tracer should not interfere with the measurement of the analyte, and
- Chemical equilibrium between the tracer and analyte should be established at the earliest possible point in the analysis.

Furthermore,

- The tracer should not be present in the samples being analysed,
- The tracer should be pure and not introduce contamination into samples being measured, and
- The tracer activity should be traceable to national or international standards.

For the analysis of technetium, the analyst has a choice of four technetium isotopes: \(^{99m}\)Tc, \(^{99}\)Tc, \(^{98}\)Tc and \(^{98m}\)Tc. The scarcity of \(^{97}\)Tc and \(^{97m}\)Tc effectively restricts the choice of the analyst to \(^{99m}\)Tc and \(^{99}\)Tc, both of which have been employed in the analysis of technetium. Additionally, the stable element thoria has been employed as a tracer for technetium (Harvey et al., 1991), but the potential for chemical speciation means that this is not necessarily the optimum approach. Technetium-99 m has the advantage of being widely used in medical imaging and is therefore produced on a large scale. Balanced against this is its short half-life of 6.067(10) h, which limits analysis time, and the possible contamination with \(^{99m}\)Tc to which it decays; breakthrough of \(^{98}\)Mo may potentially also be a problem, although this is avoided by careful separation of the \(^{99}\)Tc from the \(^{99}\)Mo parent. This leaves \(^{99m}\)Tc as a practical solution as a tracer radionuclide in the measurement of \(^{99}\)Tc. Technetium-99 m decays with a half-life of 6.6 ± 2 day (ENSDF, 2011) via \(\beta^-\) (0.961(32)) to stable \(^{99}\)Mo, and by \(\beta^-\) (0.0388(32)) to \(^{99m}\)Tc that in turn decays by \(\beta^-\) with a half-life of 200 ± 0.1 h to \(^{99}\)Mo. The principal \(\gamma\) emissions of \(^{99}\)Tc:

- 204.1 keV: 0.6132(13) – also from \(^{98}\)Tc: 0.00304(23)
- 582.1 keV: 0.2096(5)
- 835.1 keV: 0.2683(19)

combined with the moderately long half-life, make it straightforward to measure.

Radiochemical analysis of plutonium is also constrained by the few radionuclides suitable for tracing: \(^{239}\)Pu, \(^{238}\)Pu and \(^{244}\)Pu. Of these, there is essentially no \(^{248}\)Pu that can be obtained in a suitably pure state at present, and the supplies of \(^{244}\)Pu are limited. Plutonium-236 decays by \(\beta^-\) emission to \(^{236}\)U with a half-life of 2.858 ± 0.008 years, emitting these \(\gamma\) particles:

- 5614 keV: 0.0018 ± 0.0001
- 5721 keV: 0.3095 ± 0.0045
- 5768 keV: 0.6936 ± 0.0045

All of the photon emissions of \(^{239}\)Pu are of low abundance and low energy.

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2. Production and measurement of $^{99m}$Tc

Technetium-99 m can be produced in a variety of ways, but the optimum route is through the $\alpha$-particle irradiation of niobium metal (Harms et al., 2004). Niobium is monoisotopic with mass number 93. The advantage of using the $^{99}$Nb($\alpha$,2n)$^{99m}$Tc reaction is that there is no conceivable route by which $^{99}$Tc can be generated.

To produce $^{99m}$Tc, a single thin (0.025 m) foil was irradiated at the University of Birmingham cyclotron facility, with a total delivered charge of $0.13 \times 10^{10}$ C (or 36 $\mu$A h) with 35 MeV $\alpha$-particles. In terms of the incident $\alpha$-particles, this represents a "thick" target, since the $\alpha$-particles are stopped by the foil. The irradiated target was returned to NPL for processing and measurements. Previous work at NPL (Harms et al., 2004) had found that the dissolution of niobium could be rather tedious in that a mixture of hydrofluoric acid and nitric acid was employed to dissolve the irradiated target; this dissolution technique generates heat and is thus self-accelerating, unless the container in which the dissolution takes place is cooled. Consequently, for this work, the irradiated target was placed in 10 mL concentrated hydrofluoric acid and nitric acid solution, and the $^{99m}$Tc was eluted by the evaporation of 1 mL aliquots. Although the dissolution technique was the same, slow addition of concentrated nitric acid allowed heat to be dissipated and therefore better control of the dissolution was achieved. The resulting solution was used directly to prepare liquid sources for $\gamma$-ray spectrometry. The activity of the dissolved target was such that $\sim 10^{-1}$ dilution of the target solution was carried out to prepare the 4 $\gamma$-spectrometry sources. This dilution meant that the hydrofluoric acid was not concentrated enough to appreciably degrade the glass ampoule in the short term (10-20 days).

Activity measurements to determine the $^{99m}$Tc content of the irradiated foil were carried out using NPL’s high-resolution high-purity germanium spectrometers calibrated for 1 mL aqueous solution in a 2 mL ampoule. The ampoule was placed on an optical bench at 15 cm from the end cap. The detector efficiency curve was derived from measurements of single radionuclide solutions that were either calibrated on the NPL ionisation chambers or generated from solutions which were standardised by absolute techniques at NPL.

3. Production and measurement of $^{238}$Pu

As noted earlier, the production of $^{238}$Pu is rather complex, in that there is no direct way to produce this radionuclide. Four cyclotron production routes were employed:

- $^{238}$U($d$,4$n$)$^{232}$Th($p$)$^{238}$Pu (Rufford et al., 1990), 99.98$\%$, 4.3$C$ (1.2 m $\mu$A h).
- $^{238}$U($d$,4$n$)$^{234}$Th($p$)$^{238}$Pu (Ashdown et al., 2005), 99.74$\%$, 2.1$C$ (400 $\mu$A h).
- $^{238}$U($d$,2$n$)$^{236}$Th($p$)$^{238}$Pu (Bellido et al., 1993), 99.94$\%$, 2.1$C$ (400 $\mu$A h).
- $^{238}$U($d$,4$n$)$^{234}$Th($p$)$^{238}$Pu (Bellido et al., 1994), 99.82$\%$, 2.0$C$ (800 $\mu$A h).

In each case the incident particle (proton or deuteron) energy was 20 MeV and the beam time integrated current was assumed to have a 5% uncertainty. Targets were prepared by the evaporation of uranyl nitrate ($UO_2(NO_3)_2$) solution onto a copper target substrate, except for the $^{238}$U irradiation, where uranium metal foil was employed. In all cases, a titanium cover foil was used to contain any loose material and each target contained $\sim$1 g of uranium. Irradiation was carried out as before, using the proton or deuteron beam lines as appropriate.

The irradiated target was returned to NPL for chemical processing, which was carried out in a portable glove box. The dissolution of the targets was straightforward, water being used to dissolve most of the uranyl nitrate and nitric acid to dissolve any uranium oxides that were formed during irradiation. The irradiated targets contained up to 1 kg of short-lived fission products, making handling of the material quite restrictive. Portions of the dissolved target were taken and further diluted for $\gamma$-ray spectrometry, and portions of this solution were used to measure the $^{238}$Pu content.

Plutonium-236 was separated by adding calibrated $^{242}$Pu tracer to the sample and separating plutonium from the solution by anion exchange chromatography (Körhö, 1989). A straightforward procedure was then followed in which the material was converted to the chloride form by evaporation with concentrated hydrochloric acid; the residue was dissolved in 9 M hydrochloric acid and this solution was used to adsorb uranium and plutonium onto a Bio-Rad AG5-X8 anion resin (100-200 mesh). The column was further washed with 9 M hydrochloric acid, then 7.2 M nitric acid to remove the bulk of the fission products. Finally, a 6 M hydrochloric acid wash was used to remove $^{238}$U. Plutonium was eluted from the column with 0.1 M ammonium iodide (iodide reduces plutonium, but not uranium or neptunium, to the Pu$^{4+}$ ion which is not adsorbed by anion resin). Despite the efforts to remove all the fission products, there was some residual $^{242}$Pu found in the plutonium fraction; further purification was deemed unnecessary, since this would not interfere with the $\alpha$-spectrometry measurements. The plutonium-containing eluate was evaporated to dryness at 90 °C, and then redissolved in 5% (v/v) sodium hydroxide solution with 15% sodium sulphate and electrosprayed onto a tantalum substrate. The resulting sources were then measured by $\alpha$-particle spectrometry (Kreissl, 1977).

4. Results for $^{99m}$Tc

The irradiated target was found to contain these nuclides at the end of the irradiation:

$^{99m}$Tc: 1.6(6) MBq/t 10.15(4) days
$^{99}$Tc: 3.17(7) MBq/t 6.14(4) days
$^{99m}$Tc: 110(2) MBq/t 4.28(7) days

After one half-life of $^{99m}$Tc, the $^{99}$Tc activity had decayed to ~0.4% of the $^{99m}$Tc activity and $^{99}$Tc had decayed to ~1.6%.

Since the target was irradiated with 0.11%10(10) C (36 $\mu$A h) $\alpha$-particles, a thick target yield of 24.4 ± 2.8 MBq/MB. This can be derived from the yield for $^{99m}$Tc from the $^{99}$Th($\alpha$,n)$^{99m}$Tc reaction is $850 ± 90$ MBq/MB.

5. Results for $^{238}$Pu

The irradiated targets contained the following $^{238}$Pu at the end of irradiation:

$^{238}$Pu($d,n$): 150(10) kBq/t $^{238}$Pu/$^{238}$Pu ratio = 0.00032(2)
$^{238}$Pu($d,n$): 24.8(4) kBq/t $^{238}$Pu/$^{238}$Pu ratio = 0.001
$^{238}$Pu($d,2n$): 440(1 1) kBq/t $^{238}$Pu/$^{238}$Pu ratio = 0.002
$^{238}$Pu($d,3n$): 518(84) kBq/t $^{238}$Pu/$^{238}$Pu ratio = 0.015(2)
From this data, the following thick target yields can be calculated:

\[
\begin{align*}
\text{\textsuperscript{231}}U(d,n) &: 34.8 \ (2.5) \ \text{kBq/C} \\
\text{\textsuperscript{232}}U(p,n) &: 175(35) \ \text{kBq/C} \\
\text{\textsuperscript{238}}U(d,2n) &: 314(79) \ \text{kBq/C} \\
\text{\textsuperscript{238}}U(p,3n) &: 180(30) \ \text{kBq/C}
\end{align*}
\]

6. Conclusions

Through irradiation with a cyclotron, useable thick target yields for the production and purification of \textsuperscript{95m}Tc and \textsuperscript{239}Pu have been established. This will enable NPL to produce these radioanalytical yield tracers within 3 months of a request to make the material.

For \textsuperscript{95m}Tc, the remaining issue is to reduce the \textsuperscript{96}Tc yield, whilst retaining the ability to produce reasonable quantities of \textsuperscript{95m}Tc. Future work with thinner targets should answer this question. As far as the production of \textsuperscript{239}Pu is concerned, the work has identified the route that gives the highest purity material, although this is not necessarily the highest yield route to this nuclide. In both cases, additional work is needed to reduce the large uncertainties attendant on the thick target yields.

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