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PRODUCTION OF ^{117m}Sn WITH A HIGH SPECIFIC ACTIVITY BY RECOIL

By

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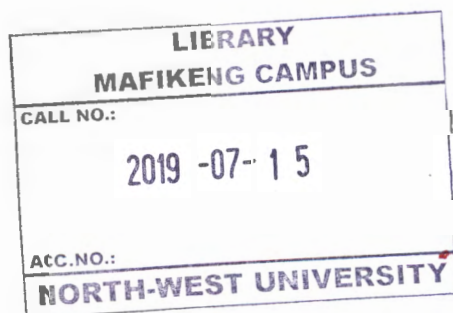
Declaration of Authenticity

I, the undersigned KEFILWE THATO THOANE, hereby certify that the work presented in this dissertation except where otherwise indicated, is my own original work and has not been submitted to any university for the purpose of obtaining a degree.

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Ms KEFILWE THATO THOANE

Acknowledgements

Abstract

The radionuclide ^{117m}Sn is a promising radioisotope that is used for therapeutic applications because of its nuclear properties. The radionuclide ^{117m}Sn can be produced in a nuclear reactor or an accelerator. ^{117m}Sn can be produced in different ways, namely by a neutron capture reaction ^{116}Sn (n, γ) ^{117m}S or an elastic neutron scattering reaction ^{117}Sn (n, n', γ) ^{117m}Sn. The major hindrance is the low specific activity (Bq/mg) obtained which limits the therapeutic application thereof. In this study, tin(IV) oxide (SnO$_2$), activated carbon and graphite as recoil capture medium, were irradiated in the SAFARI-1 nuclear reactor to produce the radionuclide ^{117m}Sn. The product ^{117m}Sn was separated from the target material by solid-liquid extraction. The tin oxide and the activated carbon or graphite are chemically inert, which allowed for the extraction of the recoil atoms with relative ease using a mixture of concentrated sulphuric acid and nitric acid. Some of the targets such as SnO$_2$(C) pellet (C)/graphite flake pellet, SnO$_2$(C) pellet/graphite flake, and SnO$_2$(C) pellet/activated carbon were irradiated in the SAFARI-1 reactor for 24 h, the activity of the targets were measured using a Capintec CRC-15R calibrator before the extraction process. The activities of the targets were 0.17, 0.18, and 0.10 MBq. After the extraction process the activities of the targets were measured using γ-spectroscopy and the total tin content was determined using ICP-OES. The specific activity of the respective targets was 0.20, 0.20, and 0.50 MBq/mg for tin oxide and 0.22, 0.23, 0.08 MBq/mg for the recoil capture media. The enrichment factors of the tin oxide, activated carbon, and graphite were too low to measure. The enrichment factor for tin oxide was 1.18, 1.11, and 5.00 and for the recoil capture media 1.41, 1.29, 0.80 respectively. The enrichment of SnO$_2$ exceeds that of their respective recoil capture media values, which could be due to a possible recoil stabilization effect brought about by the recoil capture media.

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Abbreviations and Symbols

LET	Linear Energy Transfer
RT	Reactor Trip
SI	International System of Units
KeV	Kilo electron Volt
MBq	Mega Becquerel
EOB	End of Bombardment
MeV	Mega electron Volt
GE	General Electric
MeV	Mega electron
PET	Positron Emission Tomography
HFIR	High-Flux Isotope Reactor
BR2	Belgian Reactor
ATR	Advanced Test Reactor
NRU	National Research Universal
HFBR	High-Flux Beam Reactor
MURR	Universal of Missouri Research Reactor
Necsa	South African Nuclear Energy Corporation SOC Ltd
RIAR	Research Institute of Atomic Reactors
ORNL	Oak Ridge National Laboratory
ETRR-2	Egyptian Research Reactor
HPGe	High Purity Germanium detector
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy

CHAPTER 1: INTRODUCTION

1.1 Introduction

Radioactive isotopes such as ^{131}I, ^{89}Sr, ^{153}Sm, ^{186}Re, ^{90}Y, ^{32}P, ^{188}Re, ^{177}Lu and ^{117m}Sn have been widely applied and investigated in nuclear medicine for internal radiotherapy of different human diseases for many years. This is because of their accessibility and because each radionuclide have unique nuclear properties such as half-life, mode of disintegration, energy of the emitted particles and photons (Kyu et al., 1999). Each radionuclide has unique nuclear characteristics and physical properties that match a specific radiotherapy treatment. Different modes of disintegration at different rates makes each radionuclide unique (Srivastava et al., 2007). There are different radiotherapy applications that are used to treat human diseases and some of these applications are tumour therapy, treatment of arthritis, inhibition of coronary Restenosis, and angioplasty (Ponsard et al., 2009).

The half-life of the radionuclide is used to determine the initial dose and therefore the total amount of radioactivity to be administered. A too long half-life creates obvious problems in environmental safety in case of a spill or the early death of the patient. A very short half-life is problematic for shipment and shelf life concerns (Srivastava, 2004). However, the optimal half-life is 7-14 days (preferably with suitable daughter products).

The most widely used therapeutic radionuclides for bone metastasis are β-emitters such as ^{89}Sr and ^{153}Sm. Depending on the type of particle energy, β-emitters are important for solid tumours. β-emitters have a long range of penetration compared to other emitters such as alpha and auger electron emitters.

α-emitting radionuclides such as ^{211}At and ^{212}Bi are good for tumour therapy because of their high Linear Energy Transfer (LET) and thus high cytotoxicity. They are useful for treatment of single cancer cells in circulation and small cancer cell clusters (Zhernosekov, 2006). However, there are only a small number of α-emitting radionuclides which can be useful for medical applications. Most α-emitters are heavy elements that decay to radioactive, long-lived daughter products, such as ^{223}Ra (radium-223), which is primarily an α-emitter with a 95.3% fraction of energy emitted as α-particles. The external radiation exposure associated with the handling of a patient dose is expected to be low, because the typical treatment activity will be below 8 000 kBq (216 µCi) (FDA-1088).

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Auger electron emitters such as ^{67}Cu and ^{125}I belong to another intriguing class of therapeutic agents which is still under consideration. The biological significance of Auger electrons was not appreciated for many years because of their low energy level (0.01 to 100 keV) (Hofer et al., 1969, 1971) However, the Auger effect was found to be critically dependant on the cellular location of the radionuclides. Auger electron emitters located outside the cell nucleus are relatively non-toxic whereas the intracellular decay at the DNA level causes high LET-type cellular damage. It requires a particular pharmacological strategy to deliver the radionuclide into the cell and to approach the cell nucleus.

α-emitting radionuclides have been the subject of considerable investigation as cancer therapeutics. α-emitting radionuclides have the advantage of high potency and specificity. These advantages arise from the densely ionizing track and short path length of the emitted positively charged helium nucleus in tissue. Improved chemical labelling and stability is needed to achieve the desired bio-distribution and associated dose distribution necessary for successful therapy with acceptable acute and long-term toxicities. These limitations have not yet slowed the development and clinical use of α- emitter targeted therapy relative to the use of β-emitting radionuclides, but may do so in future. The short range of α-particles and distribution of α-emitters should be taken into consideration on the scale of human organ dimensions (IAEA- TECDOC-1549, 2007).

Cancer begins when cells in a part of the body start to grow out of control. There are different types of cancer, but they all start because of uncontrolled accelerated growth of abnormal cells. Cancer cells that relocate to other parts of the body, where they begin to grow and form new tumours that replace normal tissue are called metastasis (Mandeep et al., 2007). Metastasis to bone is a complex multistep process, which involves a bidirectional interaction of the tumour cells with cellular elements in three different microenvironments: the site of primary neoplasm, the circulation, and the bone microenvironments (Mandeep et al., 2007).

The main goal of treating metastatic bone disease is either to prevent a bone lesion from developing or to limit the progression of an established bone metastasis. There are two types of treatment of bone metastases, systemic and local treatments (Mandeep et al., 2007). There are different therapy treatments that can be used to cure human diseases such as chemotherapy, hormone therapy, or other medicines that are taken by mouth or injected into the arteries. These treatments can be used if the cancer has spread to only a single bone, or if there is one or a few areas of cancer sites that are more advanced than others and require

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treatment right away. In these treatments and therapies, the radionuclides listed in Table 1.1 play a major role.

The radionuclides listed in Table 1.1 are used for bone pain palliation due to their unique nuclear characteristics and play a role in different treatment radiotherapies, but ^{117m}Sn in particular has attractive nuclear properties. These include a half-life of 13.6 days and gamma energy of 159 KeV (86%). The radionuclide emits low energy conversion electrons that deposit intense energy (127, 129, 152 KeV) within a short range (0.22-0.29 mm) and which can destroy tumours with little damage to the bone marrow and healthy tissue (Ponsard et al., 2009). Radionuclides such as ^{153}Sm and ^{186}Re are also compatible for the use in bone pain; however their half-lives are shorter.

Table 1.1 Radionuclides suitable for bone palliation with their nuclear properties and characteristics (Srivastava, 2004)

Radionuclides	Half-life (days)	Maximum β⁻ energy (MeV)	Average β⁻ energy (MeV)	Average penetration in soft tissue (mm)	Gamma photons (abundance) (KeV)
Erbium-169	9.40	0.34	0.10	0.30	-
Holmium-166	1.12	1.84	0.67	3.30	81 (6%)
Lutetium-178	6.71	0.50	0.14	0.35	208 (11%)
Phosphorus-32	14.26	1.71	0.70	3.00	-
Rhenium-186	3.78	1.08	0.35	1.05	137 (9%)
Rhenium-188	0.71	2.12	0.64	3.8	155 (15%)
Samarium-153	1.95	0.81	0.22	0.55	103 (29%)
Strontium-89	50.53	1.46	0.58	2.4	-
Yttrium-90	2.67	2.28	0.94	3.6	-
Tin-117m	13.60	0.15 CE	Conversion e⁻	0.22-0.29	159 (86%)
Radium-223	11.43	5.75 α	α particle	< 0.01	154 (6%)

1.2 Production of radionuclides

Radionuclide production involves altering the number of photons and or neutrons in the nucleus of the target. If a neutron is added without the emission of particles, then the resulting nuclide will have the same chemical properties as those of the target nuclide. If however, the target nucleus is bombarded by a charged particle, for example a proton, the resulting nucleus will usually be that of a different element. There are many sources for the production of radionuclides, amongst them are nuclear reactors and particle accelerators (cyclotrons) (IAEA-TECDOC-1340, 2003).

The main advantage of an accelerator compared to a nuclear reactor is that they can produce radionuclides with high specific activities, reactions such as (p, xn) and (p, α). Also less radioactive waste is produced when an accelerator is used for production of charged particle reactions as observed when targeting ^{11}B (boron) with ions accelerated in a cyclotron while nuclear reactors generate a high volume of radioactive waste (Kahn, 2010).

Radionuclides can be produced by using a suitable target (enriched target). Examples of radionuclides produced in an accelerator are listed in Table 1.2. For many years accelerators have been used to create proton rich artificial radionuclides. Among different accelerator principles and constructions, cyclotrons are the most widely used for medical purposes. A cyclotron is the simplest cyclic accelerator, which belongs to the class of resonance accelerators (Zhernosekov, 2006).

Table 1.2 Some cyclotron-produced radionuclides used in nuclear medicine (Zhernosekov, 2006)

Product	Decay Mode	Nuclear Reaction	Natural Abundance of Target Isotopes (%)
^{11}C	β^+	$^{10}B(d, n)^{11}C$	19.7
		$^{11}B(p, n)^{11}C$	80.3
^{13}N	β^+	$^{12}C(d, n)^{13}N$	98.9
^{15}O	β^+	$^{14}N(d, n)^{15}O$	99.6
^{18}F	β^+, EC	$^{20}Ne(d, \alpha)^{18}F$	90.9
^{22}Na	β^+, EC	$^{23}Na(p, 2n)^{22}Na$	100
^{43}K	(β^-, γ)	$^{40}Ar(\alpha, p)^{43}K$	99.6
^{67}Ga	(EC, γ)	$^{68}Zn(p, 2n)^{67}Ga$	18.6
^{111}In	(EC, γ)	$^{109}Ag(\alpha, 2n)^{111}In$	48.7
		$^{111}Cd(p, n)^{111}In$	12.8
^{123}I	(EC, γ)	$^{122}Te(d, p)^{123}I$	2.5
		$^{124}Te(p, 3n)^{123}I$	4.6
^{201}Tl	(EC, γ)	$^{201}Hg(d, 2n)^{201}Tl$	13.2

The most significant advantage of the cyclotron is production of the relative short-lived Positron Emission Tomography (PET) radionuclides such as ^{18}F ($T_{1/2}$ = 109.7 min) and ^{11}C ($T_{1/2}$ = 20.38 min). Due to the half-life of these isotopes they are often produced and used in in-house installed facilities. In all cases sufficient activity can be produced on small medical cyclotrons with 11-18 MeV proton energy with a beam current of 10-100 μA.

Research reactors represent important facilities for production of therapeutic radioisotopes. The irradiation of stable isotopes in nuclear reactors results in the neutron capture nuclear reaction (n, γ) (IAEA-TECDOC-1340, 2003).

Neutron irradiation of fissionable materials, such as ^{235}U, induces a fission process that is splitting the nucleus into two or more smaller nuclei with maximum mass distribution of

about 94 and 138. Fast neutron irradiation is able to cause (n, p) nuclear reactions and is useful in some cases. A radionuclide can be produced in a nuclear reactor where a neutron flux is used to irradiate a target in which neutron capture converts the target material into the radionuclide of interest. Different chemical treatments can be used to separate or extract a target material from a product material (radionuclide of interest).

Table 1.3 shows some useful radionuclides which can be produced in nuclear reactors along with the production route and cross section for thermal neutron capture nuclear reactions (Mirzadeh et al., 2003).

Table 1.3 Reactor produced diagnosis and therapeutic radionuclides (Zhernosekov, 2006)

Radionuclides	Half-life ($T_{1/2}$)	Production	Thermal cross section (σ_{th}) [barn cm^2]	Application
^{64}Cu	12.70 h	^{63}Cu(n, γ)	4.5	PET/RT
		^{64}Zn(n, p)	Fast neutrons	
^{67}Cu	61.7 d	^{67}Zn(n, p)	Fast neutrons	RT
^{177}Lu	6.71 d	^{176}Lu(n, γ)	1780	RT
		^{176}Yb(n, γ) β^-	3	
^{161}Tb	6.91 d	^{160}Gd(n, γ) β^-	1.5	RT
^{166}Ho	26.80 h	^{165}Ho(n, γ)	61	RT
		^{164}Dy(n, γ) β^-	2700	
		^{165}Dy(n, γ) β^-	3500	
^{153}Sm	1.95 d	^{152}Sm(n, γ)	206	RT
^{149}Pm	53.1 h	^{148}Nd(n, γ) β^-	2.5	RT
		^{235}U (n, fission) (1.074 %)		
^{175}Yb	4.2 d	^{174}Yb(n, γ)	100	RT
		^{98}Mo(n, γ)	0.14	RT
^{99}Mo	65.94 h	^{235}U(n, fission)		RT
^{117m}Sn	13.6 d	^{116}Sn (n, γ)	600	
		^{117}Sn(n, ˙n, γ)	105	

1.3 Specific activity

The specific activity is a measure of the number of radioactive atoms or molecules as compared with the total number in the sample, and is usually expressed in terms of radiation per mass. The SI unit is Bq/mol, although the traditional units have been Ci/gram (Ci/g). The specific activity of an isotope or radiopharmaceutical is important in determining the chemical and biological effect the substance may have on the system under investigation.

The specific activity or concentration of radionuclides is a very important factor whilst working with radionuclides, as important as low solubility in the chemical industry. The proper specific activity of a given radiopharmaceutical depends on the concentration or activity of the target molecules, such as specific receptors, enzymes, proteins, or genes present in a given cell or tissue.

$$SA = \frac{A}{m} \qquad\qquad 1.1$$

Where SA is the Specific Activity, A is the Activity and m is the mass.

Specific activity is also an important parameter since in many cases the availability of very high specific activity or carrier-free radioisotopes is required for biological applications. One example of the importance of high specific activity is the radiolabeling of tumor-specific antibodies for both diagnostic and therapeutic applications where only a very small amount of radiolabelled antibodies are administered to ensure maximal uptake at the limited tumor cell surface antigen site (Welch et al. 2002).

There have been many researchers trying to produce ^{117m}Sn with a high specific activity using different types of nuclear reactions. Toporov et al. (2005) investigated the production of ^{117m}Sn with a high specific activity by irradiating enriched (up to 92 %) metallic tin as a target in the core of the reactor for an irradiation period of 24 h. After irradiation of the target, it was dissolved in hydrochloric acid to reduce the metal in a hydrogen atmosphere. An anion exchange process was used for purification. The activity of the product was measured using an HPGe detector. The specific activity achieved for ^{117m}Sn was higher than 17 Ci/g in a stationary medium size reactor (SM). There have also been other attempts to produce ^{117m}Sn with high specific activity. Mirzadeh et al. (1997) investigated the production of ^{117m}Sn, ^{119m}Sn, and ^{195m}Pt using a neutron inelastic scattering reaction, by irradiating ~10 mg of

highly enriched targets of Sn (as SnO_2) and metallic platinum in a High-Flux Isotope Reactor (HFIR) for 1 h irradiation time. The targets were cooled after irradiation and then soaked in concentrated nitric acid for a few minutes and the measurements were taken using an HPGe-γ-ray detector. The specific activities obtained were 1.4 MBq/mg for [195m]Pt, 3.3 MBq/mg for [117m]Sn, and 4.4 MBq/mg for [119m]Sn. The irradiation time was increased to one cycle (21 days) at 85 MW power level, the expected specific activities were 5.2×10^2 and 3.1×10^2 MBq/mg (14 and 8.5 mCi/mg) for [117m]Sn and [119m]Sn respectively and for [195m]Pt 6.3×10^2 MBq/mg (17.1 mCi/mg). The irradiation time, cross section, neutron flux and the power of the reactor have an effect on the specific activity of the product. The specific activity of each radioisotope seems to differ with a change in irradiation time. Different reagents and separation methods are used to purify the product and each method has its own advantages and disadvantages.

A high specific activity of 23.1 ± 1.9 Ci/mg was achieved after irradiating enriched [117]Sn for a period of 35.1 days using the inelastic neutron scattering [117]Sn (n, n') [117m]Sn reaction (Maslov et al., 2011). Enriched [117]Sn target material was irradiated for 100 h, operating at an energy of 50 MeV α-particle beam energy and a beam current of 50 µA (Maslov et al., 2011). The activity of [117m]Sn obtained was 7×10^{10} Bq. The use of enriched targets and purified material has an effect on the specific activity in a positive way, such that it produces the radioisotope of interest with a high specific activity and minimal impurities. Impurities are usually found in commercial targets which are used to produce the required isotopes by neutron irradiation. These impurities are formed either by neutron capture reactions or threshold reactions or both (Maslov et al., 2011).

A weighed amount of 36.2 mg of target material of tin oxide (SnO_2) with purity of 99.99% was irradiated for 3 h in a research reactor (ETRR-2) and after irradiation the sample was left to cool before chemical processing and measurements were performed (Mirzadeh et al., 1994). The sample was transferred into clean polyethylene vials for gamma ray measurements and high yields of the product [117m]Sn were obtained. Mirzadeh et al. (1994) investigated the production of [117m]Sn by irradiating 16 mg of [117m]Sm as target material in an 85 MWt power level HFIR for a 1 h irradiation period. The experimental specific activity achieved was 14.0 mCi/ mg for [117m]Sn.

[117m]Sn radionuclides (8.18 Ci/mg) can be obtained, depending on the production route, in either a no-carrier-added form or a carrier-added form. The no-carrier-added form means a

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radionuclide without any addition of stable isotopes of the same element (specific carrier in the system), while carrier-added considers the presence (generally unwished or added for some reasons) of stable isotopes. Radionuclides produced with no-carried added, will have high specific activities because there are no stable isotopes that might affect the specific activity of the product, while the radionuclide produced with carrier added, will have a lower specific activity because of the stable isotopes added to the product such as other radionuclides produced with the radionuclide of interest. High specific activity can be obtained by separating the accelerator-produced radionuclide from the irradiated target (Birattari, 2001) and also by using an enriched target and high neutron flux.

1.4 Carrier-free

Radioactive preparations in which no carrier is intentionally added during the manufacture or processing may be referred to as carrier-free. The designation no carrier-free-added is sometimes used to indicate that no dilution of the specific activity has taken place by design, although carrier may be present due to the natural presence of a non-radioactive element or compound accumulated during the production of the radionuclide or preparation of the compound in question.

Carrier-free specific activity can be determined by a consideration of the relationship between activity A, the number of radioactive atoms present N, and the decay constant λ, where $\lambda = 0.693/T_{1/2}$.

$$A = N\lambda = N\left(\frac{0.693}{T_{1/2}}\right) \hspace{4cm} 1.2$$

The specific activity of radioactive materials that are not carrier-free can be determined by measuring both the radioactivity and the total amount of the element or compound of interest. Accurate determination, where a material has a high specific activity, may be difficult due to limitations in obtaining an accurate determination of the amount of the substance present by standard physical or chemical analysis.

1.5 Production of ^{117m}Sn

The radionuclide ^{117m}Sn can be produced in a nuclear reactor or an accelerator. In a nuclear reactor ^{117m}Sn can be produced in different ways, namely in a neutron capture reaction ^{116}Sn (n, γ) ^{117m}Sn or an elastic neutron scattering reaction ^{117}Sn (n, n', γ) ^{117m}Sn. The first reaction does not produce ^{117m}Sn with high specific activity due to a low neutron capture cross section. The second reaction can produce ^{117m}Sn with higher specific activity, because the

threshold of this reaction ^{117}Sn (n, n', γ) ^{117m}Sn takes place in a high flux where the energy of the fast neutron is high enough ($E_n > \sim 0.1$ MeV, E_n is the energy of the neutron).

The reported specific activity of ^{117m}Sn is currently 20 Ci/g (~87.83 GBq/mmol) at the end of bombardment (EOB) or irradiation (Jansen, 2010). There have been many attempts to produce ^{117m}Sn with a higher specific activity in a nuclear reactor and accelerator. Several methods have been attempted to produce ^{117m}Sn with high specific activity using a proton induced reaction on ^{114}Cd, ^{115}In, and ^{115}Cd in an accelerator, but all of these reactions gave low yields. Srivastava (2007) used an accelerator to produce ^{117m}Sn with high specific activity with cross section of 5 mb and proton energies of 38 to 60 MeV. The specific activity that was attained was 30 Ci/g.

Historically, nuclear recoil was observed in many nuclear reactions, and gave rise to numerous studies on enrichment of radionuclides in different compounds. Mausner et al. (1992) used tetraphenyl tin (Figure 1.1 compound 4) as target and a neutron capture reaction was used. The enrichment factor of the product ^{117m}Sn was low compared to ^{113}Sn. Organotin compounds (Figure 1.1) can also be used to produce ^{117m}Sn with high specific activity by recoil. The Szilard Chalmers process (Szilard & Chalmers, 1934) is a technique that can be utilized to improve the specific activity of (n, γ) produced radionuclides. The Szilard Chalmers process depends upon the fact that, following neutron absorption, prompt gamma rays are emitted which may cause nuclear recoil and subsequent molecular bond disruption. This excitation sometimes leaves the resulting hot atom in a different chemical state from unreacted atoms and thus chemically separable. This separated fraction is relatively "unriched" in radioactive atoms and has higher specific activity than the rest of the target. The SA unit of atom % is defined as follow:

$$SA \ (unit \ in \ atom \ \%) = \frac{100X \ Hot \ atom \ numbers \ of \ a \ specified \ radionuclide}{Atom \ numbers \ of \ the \ chemical \ element \ of \ specified \ radionuclide}$$

This can be formulated as follows:

$$SA(atom \ \%) = 100 . N_{Ri \ (A)} / N_A \qquad\qquad 1.3$$

SA in units Bq/Mol and Bq/g are currently used. The conversion between the SA units is the following:

$$SA\ (Bq/g) = \frac{SA\ (Bq/Mol)}{M_{iA}} = \frac{100.N_{Ri(A)}.\lambda}{100\ N_A\ (6.022X10^{23})^{-1}\ M_{iA}}$$

$$= SA\ (atom\ \%)\frac{\lambda_{Ri(A)}6.022X10^{21}}{M_{iA}}$$

$$SA\ (Bq/Mol) = SA(Bq/g)M_{iA} = 6.022X10^{23}\lambda_{Ri(A)}SA\ (atom\ \%) \qquad 1.4$$

Where M_{iA} is the atomic weight of the target or radioactive material of given isotopic composition of the chemical element A.

For a radioactive material containing n isotopes of the element A:

$$M_{iA} = \sum_i^n P_{N_{n,A}}/\sum_i^n (P_{N_{n,A}}/M_{N_{n,A}})$$

Where $P_{N_{n,A}}$ and $M_{N_{n,A}}$ are the weight percentage and atomic weight of the isotope $N_{n,A}$, respectively.

$$SA_{carrier-free}(Bq/Mol) = \frac{N_{Ri(A)}\lambda_{Ri(A)}}{N_{Ri(A)}/6.022X10^{23}} = 6.022X10^{23}\lambda_{Ri(A)} = \frac{4.1732X10^{23}}{T_{1/2}} \qquad 1.5$$

Identifying Eq.1.4 with Eq.1.5 (individually M_{iA} as the atomic weight of the concerned radioisotope), it is clear that the SA of a carrier-free radionuclide in unit atom % of 100%. (Van So Le. 2011)

The radionuclide of interest [117m]Sn could be produced by adapting a Szilard-Chalmers reaction, where the main objective of the Szilard-Chalmers process or reaction is to produce radioisotopes with high specific activity with no impurities. Most medical radioisotopes that are produced via neutron capture (n, γ) reaction emit gammas, and the nucleus receives some recoil energy in this process.
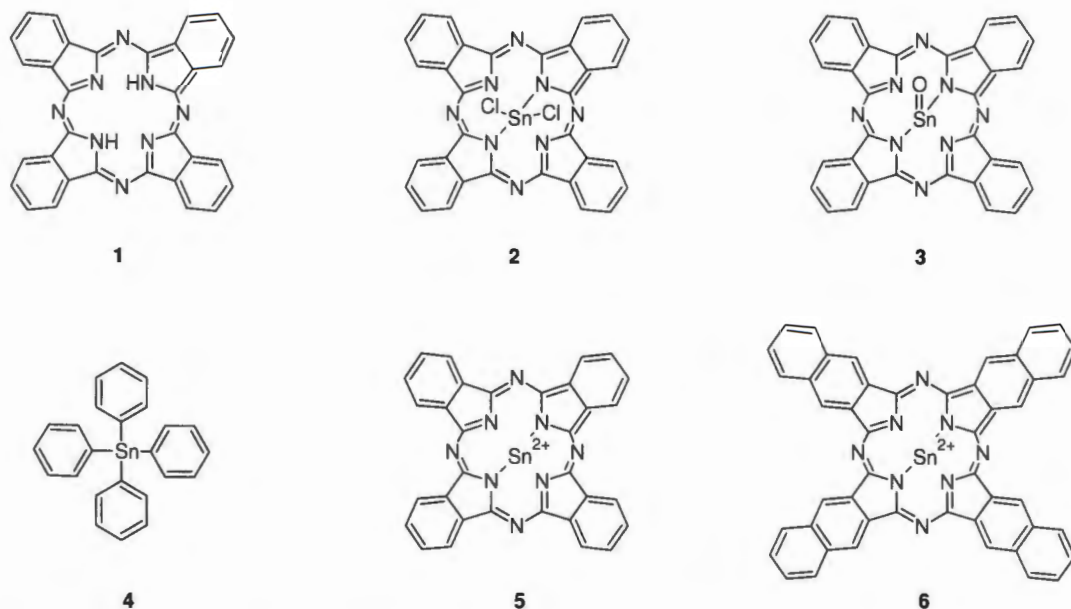
Fig. 1.1 Phthalocyanine **1**, **4**-tetraphenyl tin and organotin compounds **2**, **3**, **5** and **6**

1.6 Objectives

1.6.1 Aim

The aim of this project is to investigate the possibility of obtaining ^{117m}Sn with high specific activity (Ci/g) for application in radiotherapeutic pharmaceuticals for the treatment of internal bone metastases. The proposed method should produce ^{117m}Sn by the following reaction ^{116}Sn (n, γ) ^{117m}Sn in a nuclear reactor. However, due to the similar chemistry of product and starting material, the isolation of the ^{117m}Sn activity presents a challenge. If ^{117m}Sn could be ejected from the crystal lattice of the irradiated starting material during the nuclear reaction, it might be possible to selectively capture the product in the surrounding medium, thereby separating it from the starting material and therefore deliver an enriched ^{117m}Sn product.

1.6.2 Objectives

- Therefore, the first objective was to identify the optimum conditions, and the best post-irradiation separation route to prepare high specific activity (or enriched) ^{117m}Sn. If successful, the method will be scaled up and optimized for larger production quantities, which could be commercially exploited.

- To irradiate different targets of tin dioxide (SnO_2) in the SAFARI-1 research reactor.

- Activated carbon and graphite were the recoil capture media used in this study because they are less prone to irradiation damage and can withstand long irradiation

periods. The position where targets were placed for irradiation in the SAFARI-1 research reactor was the hydraulic position.

- The binding materials, namely graphite and aluminium were used.

- Aluminium powder, aluminium oxide (Al_2O_3), activated carbon and graphite were selected to determine the choice of recoil capture medium in the cold experiment prior to the hot experiment.

- The method for separating irradiated target material from the product was solid-liquid extraction.

- The extraction solvents were acids. The acids selected were nitric acid 55% (HNO_3) and sulphuric acid 32% (H_2SO_4).

- After the separation, the activity of the product was measured with γ-spectrometry and the total analysis with ICP-OES.

- The activity of the product was used to calculate the specific activity of ^{117m}Sn and the enrichment factor.

1.7 Thesis Outline

This thesis consists of five chapters. In Chapter 1 the introduction on the production of radioisotopes is given as well as a discussion of the reactors and accelerators that are used to produce those radioisotopes and the different types of nuclear reactions. The objectives of this study to produce ^{117m}Sn with high specific activity are also given. In Chapter 2 the different methods for the study of the production of ^{117m}Sn are reviewed. In Chapter 3 the experimental procedures used for the production of tin are presented. In Chapter 4 the results and discussions for the production of tin from the organotin compounds and metal oxides and metal salts of tin are examined The overall conclusions drawn from the results and the recommendations are given in Chapter 5.

CHAPTER 2: THEORY

2. 1 Theoretical background

2.1. 1 Introduction; Tin

Tin has a few important inorganic tin compounds, such as tin(II) and tin(IV) chlorides, tin(II) and tin(IV) fluorides, potassium and sodium stannates. Tin has two oxidation states, namely the +2 and +4 oxidation states, also known as tin(II) and tin(IV) which are both fairly stable (Howe, 2005).

Tin is used for the production of solder alloys, electrical alloys, and general applications. Tin may be released to the atmosphere from both natural and anthropogenic sources; it can also be released as a dust by wind storms (Howe, 2005).

2.1.2 Tin in the environment

Tin oxide is insoluble and the ore strongly resists weathering, so the amount of tin in soils and natural water is low. The concentration in soil is generally between 1 and 4 ppm and some soil have less than 0.1 ppm, while peats can have as much as 300 ppm (Howe, 2005). Tin occurs naturally in the Earth's crust, with an average concentration of approximately 2-3 mg/kg.

2.1.3 Physical and chemical properties of Tin

Tin has the atomic symbol Sn, the atomic number 50, and atomic mass of 118, 71. Tin occurs naturally as the stable isotopes ^{112}Sn (0.97%), ^{114}Sn (0.65%), ^{115}Sn (0.36%), ^{116}Sn (14.5%), ^{117}Sn (7.7%), ^{118}Sn (24.2%), ^{119}Sn (8.6%), ^{120}Sn (32.6%), ^{122}Sn (4.6%) and ^{124}Sn (5.8%). Table 2.1 contains the physical and chemical properties of inorganic compounds of tin.

Table 2.1 Physical and chemical properties of tin and some inorganic tin compounds (Howe, 2005).

Compound (formula)	Melting point (ᵒC)	Boiling point (ᵒC)	Solubility in water
Sn	232	2602	Insoluble
$SnBr_4$	31	205	Slightly soluble
$SnCl_2$	247	Decomposes between 623-652	Soluble
$SnCl_4$	-33	114	Slightly soluble (reacts with)
SnF_4	213	850	Slightly soluble
SnI_2	320	365	Slightly soluble
SnI_4	143	No data	Slightly soluble
SnO	1080	1900	Insoluble
SnO_2	1630	-	Insoluble
$Sn_2P_2O_7$	Decomposes at 400	-	Insoluble
SnS	880	1210	Insoluble

2.1.4 Redox behaviour of tin

It has been shown that Sn^{2+} is readily oxidized to Sn^{4+}. The standard electrode potentials and the half-reactions for tin are given below.

$$Sn^{4+} + 2e^- \rightarrow Sn^{2+} \qquad E° = + 1.5 \text{ V} \qquad 2.1$$

$$Sn^+ + 2e^- \rightarrow Sn \text{ (s)} \qquad E° = - 0.13 \text{ V} \qquad 2.2$$

$$Sn \text{ (s)} + 4H^+ + e^- \rightarrow SnH_4(g) \qquad E° = -1.70 \text{ V} \qquad 2.3$$
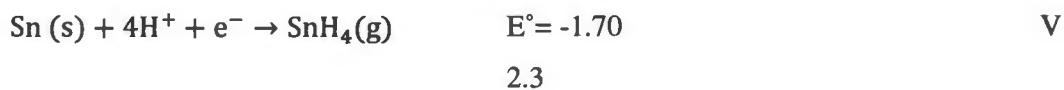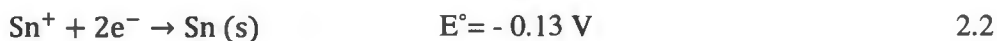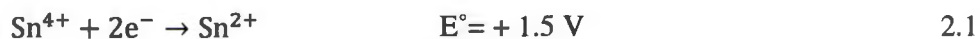
The standard electrode potentials show or explain the strongly reducing nature of the Sn^{2+} (-0.13 V) and inversely for Sn^{4+}.

2.2 Radioisotopes

Production of radioisotopes, radiolabelled compounds, radiation sources and other products based on radioisotopes constitute important activities of several national nuclear programmes (AIEA-TECDOC-1549, 2007). There are four principle radionuclide production processes namely nuclear fission (reactor breeding), neutron activation processes, charged particle induced reactions, and radionuclide generators (chemical method) (Kahn, 2010). Each of these sources produces radioisotopes in a different manner. Accelerators use charged particles to produce radioisotopes and reactors use neutrons. Medical isotopes can also be produced by electron beam (x-ray) interactions and chemical separation from longer-live parent isotopes (Fisher, 2009).

A comparison of the different resources producing radioisotopes are given in Table 2.2. Each resource has its own characteristics which differ from each other. Cyclotrons, nuclear reactors (fission) and generators produce radioisotopes with a high specific activity while nuclear reactors (neutron activation) generally do not produce radioisotopes with high specific activity (Alharbi et al., 2000).

Table 2.2 Production method (Alharbi et al., 2000)

Characteristic	Cyclotron	Nuclear reactor (fission)	Nuclear reactor (neutron activation)	Radionuclide generator
Bombarding particle	Proton, deuteron, triton, alpha	Neutron	Neutron	Production by decay of parent
Product	Neutron poor	Neutron excess	Neutron excess	Neutron poor or excess
Typical decay pathway	Positron emission, electron	Beta-minus	Beta-minus	Several modes
Typically carrier free	Yes	Yes	No	Yes
High specific activity	Yes	Yes	No	Yes
Relative cost	High	Low	Low	Low (^{99m}Tc) High (^{81m}Kr)
Radionuclides for nuclear medicine applications	^{201}Tl, ^{123}I, ^{67}Ga, ^{111}In, ^{57}Co, ^{117m}Sn	^{99}Mo, ^{133}Xe	^{32}P, ^{51}Cr, ^{125}I, ^{89}Sr, ^{153}Sm, ^{11}C, ^{131}I	^{99m}Tc, ^{81}Kr, ^{68}Ga, ^{82}Rb

2.3 Resources that produce radioisotopes

2.3.1 Accelerators

The production of radionuclides for use in biomedical procedures, such as diagnostic imaging or therapeutic treatment, is attained through nuclear reactions in a reactor or from charged particle bombardment in an accelerator (IAEA-TECDOC-465, 2008). In accelerators, the charged particle reactions use mostly protons although deuterons and helium nuclei (alpha particles) can also be used.

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Maslov et al. (2011) investigated the production of ^{117m}Sn using the ^{116}Cd (α, 3n) ^{117m}Sn reaction by irradiating 20 mg and 16.9 mg of natural cadmium (^{116}Cd) in a nuclear reactor ((FLNR), JINR in Dubna, Russia for a period of 4.5 to 7.2 h. The target was left to cool off after the irradiation period. Chemical separation was performed after the target was cooled off (Maslov et al., 2011). The specific activity of a radionuclide is affected by different factors such as the type of the target material to be used, the energy of the beam and the irradiation time and position of the target towards the beam.

Commercial cyclotrons are a type of accelerator that accelerates charged hydrogen atoms such as protons and deuterons. The energy range of the cyclotron is between 13 and 100 MeV, with a maximum current of 2 mA. Although a cyclotron is efficient and reliable it is expensive to operate. It produces proton-rich isotopes such as ^{18}F, ^{82}Sr, ^{64}Cu, ^{11}C, ^{77}Br, ^{124}I, and ^{89}Zr (Fisher, 2009).

2.3.2 Radionuclide generator

A radionuclide generator is a device for effective radiochemical separation of daughter radionuclides formed by the decay of a parent radionuclide. The goal is to obtain the daughter in a form having high radionuclidic and radiochemical purity (Zhernosekov, 2006). Essentially, every conceivable approach has been used for parent/daughter separation strategies, including solvent extraction, ion exchange, adsorption chromatography, electrochemistry, and sublimation. Most radionuclide generator systems useful for medical applications involve secular equilibrium, where the parent radionuclide has a half-life significantly longer than that of the daughter. The most widely used radionuclide generator for clinical applications is the ^{99}Mo/^{99m}Tc generator system, because of the ease of obtaining high radiochemical yields of ^{99m}Tc (Zhernosekov, 2006).

2.4 Nuclear Reactors

The first operating nuclear reactor that used natural uranium as fuel and graphite blocks as moderator (graphite reactor) was constructed in Oak Ridge, Tennessee, USA and operated from 1943 to 1963 (IAEA-TECDOC-1340, 2003). Radioisotopes produced in reactors represent a large percentage of the total number of radioisotopes used in nuclear applications. The reactor offers a large volume for irradiation. Simultaneous irradiation of several samples can be an economic advantage, and the possibility exists to produce a wide variety of radioisotopes.

Mirzadeh et al. (1997) investigated the production of ^{117m}Sn, ^{119m}Sn, and ^{195m}Pt using inelastic neutron scattering reactions, by irradiating ~10 mg of enriched targets of Sn (as SnO_2) and metallic platinum in a High-Flux Isotope Reactor for 1 h irradiation time. The targets were cooled after irradiation and soaked in concentrated nitric acid for a few minutes before measurements were taken using an HPGe-γ-ray detector. The specific activities obtained were 1.4 mCi/mg for ^{195m}Pt, 3.3 mCi/mg for ^{117m}Sn, and 4.4 mCi/mg for ^{119m}Sn. The irradiation time was increased to one cycle (21 days) at an 85 MW power level. The expected specific activity for ^{117m}Sn and ^{119m}Sn were 5.2 x 10^2 and 3.1 x 10^2 MBq/mg (14 and 8.5 mCi/mg) respectively, and for ^{195m}Pt 6.3 x 10^2 MBq/mg (17.1 mCi/mg). The irradiation time, cross section, neutron flux and the power of the reactor have an effect on the activity of the product. The specific activities of each radioisotope differ with a change in irradiation time until saturation is reached.

Research reactors that produce medical isotopes are given in Table 2.3. Each reactor has different characteristics, since the production of radioisotopes with high specific activity depends upon the neutron flux and the type of target and position of the target in the reactor (Knapp (Russ) et al. 1998, 1999)

Table 2.3 Research nuclear reactors around the world with different neutron flux and institute (Knapp (Russ) et al., 1998) (Knapp (Russ) et al., 1999)

Published approximate maximum thermal flux values neutron/cm^2/sec/10^{14}	Name of reactor	Institution	Country
50	SM2	Dimitrovgrad	Russia
12	BR2	Mol	Belgium
10	ATR	INEL	U.S
8	HFBR	BNL	U.S
5	MURR	University of Missouri	U.S
2.8	SAFARI-1	Necsa	South Africa

2.4.1 Key nuclear reactors

2.4.1.1 National Research Universal (Chalk River, Ontario)

The reactor is being operated by Chalk River Laboratories, AECL. The reactor is a 135 MW, low enriched and high enriched targets. The reactor produces isotopes such as ^{99}Mo, ^{125}I, ^{133}Xe, ^{192}Ir. The reactor is the major isotope producer in the world (Fisher, 2010).

2.4.1.2 High-Flux Isotope Reactor (HFIR, Oak Ridge, TN)

The high flux isotope reactor is operated by Oak Ridge National Laboratory for the Department of Energy. It uses highly enriched uranium fuel elements and is 85 MW, 4×10^{15} neutrons/ cm^2s^2, and takes 26 day irradiation cycles. The reactor produces isotopes such as ^{252}Cf, and ^{188W}/^{188}Re (Knapp (Russ) et al. 1999).

2.4.1.3 SAFARI-1 Research Reactor

SAFARI-1 is a 20 MW tank-in-pool type nuclear research reactor (De Beer et al., 2012). This research reactor is used to produce medical isotopes used for diagnostic purposes and therapeutic treatment of cancer and millions of people have received the benefits of medical isotopes originating from SAFARI-1.

2.5 Nuclear reactions

Nuclear reactions represent reactions between nuclei and other fundamental particles such as electrons and photons. Nuclear reactions can be produced in nature by high-velocity particles from cosmic rays, for instance in the upper atmosphere or in space. Beams of photons, mesons, muons, and neutrinos can also produce nuclear reactions. The factors that determine the type of nuclear reaction taking place and the rate of production of the product (Sahoo et al., 2006) are

- Energy of the neutrons and the neutron flux
- Characteristics of the target material
- Activation cross section for the desired reaction.

2.6 Cross section

The cross section is a useful measure of the probability for any nuclear reaction to occur (IAEA-TECDOC-1340, 2003). The unit of the cross section is barn (one barn = 10^{-24} cm^2). The value of a cross section varies with the energy of the neutrons and varies from nucleus to nucleus. There are different types of neutrons, slow neutrons, thermal neutrons, epithermal

neutrons, and fast neutrons. The slower the neutron, the greater is the probability for a reaction. Each nuclear reaction has a cross section of its own. The cross section for a particular process is defined by Equation 2.8.

$$R_i = Inx\sigma_i \qquad\qquad 2.8$$

Where,

R_i is the number of processes of the type under consideration occuring in the target per unit time,

I is the number of incident particles per unit time

n is the number of target nuclei per cubic centimeter of target,

σ_i is the cross section for the specificed process, expressed in square centimeter, and

x is the target thickness in centimeters

Table 2.4 The neutron threshold reaction cross section (Abd et al. 2009)

Nuclear Reaction	Cross Section, mb
^{182}Ta (n, p) ^{182}Ta	0.0038 ± 0.006
^{186}W (n,2n) ^{185}W	10 ± 0.7
^{181}W (n,2n) ^{182}W	3.9
^{98}Mo (n, α) ^{95}Zr	$0.00947 \pm 0.0004, 0.00857 \pm 0.00056$
^{124}Te (n, α) ^{124}Sb	0.06 ± 0.005
^{122}Te (n,2n) ^{121}Te	0.52
^{114}Sn (n, p) ^{114m}In	2.37 ± 0.2
^{120}Sn (n, α) ^{117}Cd	0.14 ± 0.01
^{120}Sn (n, α) ^{117m}Cd	0.33 ± 0.02
^{117}Sn (n, p) ^{117}In	0.13 ± 0.006
^{117}Sn (n, n) ^{117m}Sn	$140 \pm 20, 222 \pm 16, 176 \pm 14$
^{118}Sn (n, 2n) ^{117m}Sn	0.8, 1.473
^{114}Sn (n. 2n) ^{113}Sn	10

Neutron threshold reactions on the stable isotopes of the targets are sources of some impurities and may interfere with neutron capture reactions. The nuclear data of neutron

threshold reactions and their contributions to neutron capture reactions were calculated. Table 2.4 shows the cross sections of different nuclear reactions.

Productions of cross-section of the radioactive ^{117m}Sn nuclide produced through ^{nat}Sn (p, pxn) reactions are represented in Table 2.5 Total uncertainties are also given.

Table 2.5 Measured cross section of the reaction of ^{nat}Sn (p, xn) ^{117m}Sn (Young-Sik, 2007)

Energy (MeV)	Cross section ^{117m}Sn (mb)
5.6 ± 1.1	0.69 ± 0.16
8.1 ± 1.1	0.76 ± 0.17
10.2 ± 1.0	1.07 ± 0.20
12.0 ± 1.0	1.21 ± 0.21
15.5 ± 0.9	2.54 ± 0.29
16.8 ± 0.8	3.20 ± 0.35
19.6 ± 0.8	6.77 ± 0.66
22.2 ± 0.7	10.17 ± 0.97
23.3 ± 0.7	12.45 ± 1.18
25.5 ± 0.6	16.40 ± 1.54
26.5 ± 0.6	17.91 ± 1.34
28.6 ± 0.5	20.85 ± 1.55
30.5 ± 0.5	23.41 ± 1.73
32.4 ± 0.4	24.91 ± 1.84
34.2 ± 0.4	26.73 ± 1.97
35.9 ± 0.3	28.04 ± 20.7
37.6 ± 0.3	30.92 ± 2027
39.2 ± 0.3	37.99 ± 2.79

2.7 Neutron flux

A neutron flux can be defined (φ) by the total path length covered by all neutrons in one cubic centimeter during one second. To determine how many reactions will actually occur, the number of neutrons travelling through the material has to be known and how many centimetres they travel each second (IAEA-TECDOC-1340, 2003). The equation is as follows:

$$\varphi = nv \qquad\qquad 2.9$$

Where,

φ = neutron flux (neutron/cm^2/s)

n = neutron density (neutron/cm^3)

v = neutron velocity (cm/s)

The radioactivity yield can be calculated using Equation (2.10)

$$A = \frac{N\varphi\sigma\Theta(1-\exp(-\lambda t)}{\lambda} \qquad\qquad 2.10$$

Where A is the radioactivity, N is the number of target nuclei, φ is the neutron flux (cm^{-2}.s-^{1}.μA^{-1}), σ is the reaction cross section (mbarns or 10^{-27} cm^2), t is the irradiation time (s), Θ is the percentage isotopic abundance, and λ is the decay constant of the radioactive nuclei ($\lambda = \ln(2)/T_{1/2}$). In practice the radioactivity is measured by γ-spectroscopy as the photon peak area, which implies that the detector efficiency and gamma intensity should be taken into account. The result is that $N\varphi\sigma = I\varepsilon N\varphi\sigma$, where I is the gamma intensity and ε is the detector efficiency. Rewriting in terms of Avogadro's constant $N = nN_A$, where n is the number of moles = m/M$_w$, where m is the mass (g) of target atoms, and M$_w$ formula weight (g.mol^{-1}), Equation 2.10 becomes

$$A = \frac{mI\varepsilon Na\varphi\sigma\Theta(1-\exp(-\lambda t))}{\lambda Mw} \qquad\qquad 2.11$$

Assuming 100% isotopic abundance, that is enriched ^{118}Sn ($\Theta = 1$) and the γ-intensity (I) and detector efficiency (ε) as unity; the activity at end of bombardment (EOB) can be calculated, as follows

$$A = \frac{m\varphi N_a\sigma(1-\exp(-\lambda t))}{\lambda Mw} \qquad\qquad 2.12$$

The yield or specific activity can also be calculated by rearranging the following equation, as used by Bode (1996), which is an expansion of Equation 2.9 as also elaborated by Thiep et al. (2005):

$$A = \Delta N\gamma\varepsilon = \varphi_{th}\sigma_{eff}\frac{N_a\Theta w}{M}(1-\exp(-\lambda t_{irr})).\exp(-\lambda t_d)\frac{(1-\exp(-\lambda t_m))}{\lambda}.\gamma\varepsilon \qquad\qquad 2.13$$

A = net peak area

N_a = Avogadro's number (mol^{-1})

Θ = isotopic abundance of the target isotope (%)

γ = gamma ray abundance (i.e. probability of the disintegrating nucleus emitting a photon of this energy, photons per disintegration)

w = mass of the irradiated element (g)

M = atomic mass (g. mol^{-1})

ε = photopeak efficiency of detector (i.e. probability that an emitted photon of given energy will be detected and contribute to the photopeak in the spectrum).

σ_{eff} = effective cross section (mb or 10^{-27} cm^2).

φ_{th} = photon flux (cm^{-2}. μA^{-1}. s^{-1}).

λ = decay constant

t_{irr} = irradiation time (s).

t_d = decay time (s).

t_m = measuring time (s).

In the event that the cross-section and flux are unknown, re-arranging Equation 2.13 can still provide a solution for the theoretical yield as follows:

$$\frac{A}{\gamma\varepsilon(1-\exp(-\lambda t_m))\exp(-\lambda t_d)} = \varphi_{th}\varphi_{eff}\frac{N_a\Theta w(1-\exp(-\lambda t_m))}{M\lambda} \qquad 2.14$$

Note that the right hand side of the Equation 2.14 equals that of Equation 2.13 essentially by moving all the experimentally measurable or unknown, components of Equation 2.13 to the same side- in this case the left hand-side , the yield can be calculated.

The specific activity calculation can be obtained according to the following:

$$\frac{A}{w\gamma\varepsilon(1-\exp(-\lambda t_m))\exp(-\lambda d)} = \varphi_{th}\varphi_{eff}\frac{N_a\Theta(1-\exp(-\lambda t_m))}{M\lambda} \qquad 2.15$$

2.8 Types of nuclear reactions

There are different types of reactions that can be used to produce radioisotopes. Some of the major nuclear reactions that are used for radioisotopes production are given below (Sahoo et al., 2006).

2.8.1 (n, γ) reaction

This reaction is also referred to as a neutron radioactive capture and is primarily a thermal neutron reaction, but can also be induced by epithermal as well as fast neutrons, although in general the cross section is most relevant for thermal neutrons. Some of the common radioisotopes produced by (n, γ) reactions are:

^{59}Co (n, γ) ^{60}Co

^{191}Ir (n, γ) ^{192}Ir
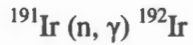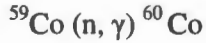
The main advantage of the procedure lies in the simple methodology and the main disadvantage in the low specific activity. The latter is improved to some extent via the Szilard-Chalmers process or via generator preparation, that is by using the decay product of an (n, γ) reaction product (Sahoo et al., 2006; Qaim, 2001).

2.8.2 (n, n', γ) Inelastic scattering

In recent years a few isometric states have been activated via the (n, n', γ) process, especially those having nuclear spin. Some of those radionuclides, for example ^{117m}In, ^{119m}Sn and ^{195m}Pt are produced in higher specific radioactivity via the (n, n', γ) process than via the (n, γ) reaction (Qaim, 2001).

2.8.3 (n, γ)-β reaction

This reaction occurs when the (n, γ) reaction produces a very short lived radioisotope, which decays by β-emission to a different radioisotope. The product can be chemically separated and high specific activity can be obtained (Sahoo et al. 2006). Examples:

^{130}Te (n, γ) ^{131}Te

^{131}Te- β⁻ + ^{131}I
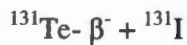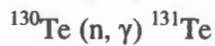
2.8.4 (n, p) reaction

In this reaction a target is bombarded with a fast neutron that lead to the emission of proton particle. Examples

^{58}Ni (n, p) ^{58}Co

^{32}S (n, p) ^{32}P
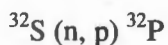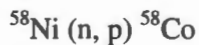
Also in this reaction a high specific activity can be obtained by chemically separating the product from the target material (Sahoo et al. 2006).

2.8.5 (n, α) reaction

This reaction is also a threshold reaction as neutrons having energy above a specific value as absorbed by the nucleus causing an α particle to be ejected; this reaction is caused by thermal neutrons. Examples

^{6}Li (n, α) ^{3}He
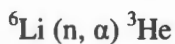
High specific activity of the product can be obtained from this reaction (Sahoo et al. 2006).

2.8.6 Fission reaction

Thermal neutron induced fission of uranium-235 provides a host of useful radioisotopes. Each fission produces two fission fragments. The fission products fall into two definite groups, one light group with mass numbers around 95 and a heavy group with mass numbers around 140. Examples

Short lived fission products – ^{99}Mo, ^{131}I

Long lived fission products – ^{137}Cs, ^{147}Pm, ^{90}Sr

This method is of great advantage and leads to no-carrier-added products that are products of very high specific radioactivity. The main disadvantage, however, is the extensive chemical processing involved (Qaim, 2001).

2.9 Radiochemical Separation Techniques

Radiochemical separations involve conventional separation techniques of analytical chemistry adapted to the special needs of radiochemistry. For example, radiochemical purity is generally more important than chemical purity (Zoltan et al., 1984). One needs to know the yield because of the availability of modern high resolution counting equipment, such as germanium γ-ray spectrometers. Modern radiochemical separations are frequently designed only to reduce the level of radioactive impurities in the sample rather than producing a pure sample (Jansen, 2010).

There are different types of radiochemical separation techniques such as precipitation, solvent extraction, exchange chromatography, fractional crystallization, distillation and volatilization, electrolysis or electrochemical deposition, and recoil separation. The separation technique that will be used in this research is recoil separation.

2.9.1 Extraction

Extraction is the withdrawing of an active agent or a waste substance from a solid or liquid mixture with a liquid solvent. The solvent is only partial miscible with the solid or the liquid. By intensive contact the active agent transfers from the solid or liquid separated mixture (raffinate) into the solvent (extract) (Wells, 2003).

2.9.1.1 Liquid-solid Extraction

When a liquid is extracted by a solid phase of the Nernst distribution law [Equation 2.16] refers to the liquid sample, and phase B, the extracting phase, represents the solid (or solid-supported liquid) phase (Wells, 2003).

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$$K_D = \frac{[X]_B}{[X]_A} \qquad\qquad 2.16$$

K_D: Solid-supported liquid phase

$[X]_A$: Liquid sample phase

$[X]_B$: Solid sample phase

2.10 Recoil Capture Medium

2.10.1 Activated Carbon

Activated carbon, also widely known as activated charcoal or activated coal is a form of carbon which has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reaction. Activated carbon is most commonly derived from charcoal (Pradhan, 2011). Activated carbons are classified on the basis of their behaviour, surface characteristics and preparation methods bbas follows:

- Powdered activated carbon (PAC)
- Granular activated carbon (GAC)
- Extruded activated carbon (EAC)
- Impregnated carbon
- Polymer coated carbon

2.10.2 Properties of activated carbon

A gram of activated carbon may contain a surface area in excess of 500 m^2, with 1500 m^2 being readily attained. Under an electron microscope the high surface area structure of activated carbon are revealed. Individual particles are intensely convoluted and display various kinds of porosity: there may be many areas where flat surfaces of graphite material run parallel to each other, separated by only a few nanometers or so (Pradhan, 2011).

2.11 Graphite

Graphite is an allotrope of carbon, similar to diamond, the difference is that graphite is two dimensional and diamond is three dimensional. It displays a hexagonal crystalline form and is greyish black in colour. Graphite has a high thermal resistance, with a melting point of about

927 ˚C. It is thermally and electrically the most conductive of the non-metals whilst being a very good lubricant (Jansen, 2010). It is very resistant to chemical attack. Graphite is found naturally in metamorphic rocks in the form of lumps, crystalline carbon, flakes, and amorphous carbon. The majority of natural graphite is produced as flake graphite which can be further processed into powder graphite.

Graphite has the property that it can slow neutrons down without absorbing them, so uranium lumps are imbedded in a graphite matrix with appropriate spacing. The neutrons entering the graphite will be slowed down, and when they finally hit a lump of uranium it is likely that they strike a ^{235}U atom and cause fission (Liang, 2012). Under irradiation, graphite undergoes changes in its thermo-mechanical properties, especially via swelling and irradiation-induced creep, which affects the graphite's operational life time. Upon neutron irradiation a neutron will knock carbon atoms from the basal plane and cause the formation of a vacancy, as depicted in Figure 2.1. (Liang, 2012)

(a)   (b)
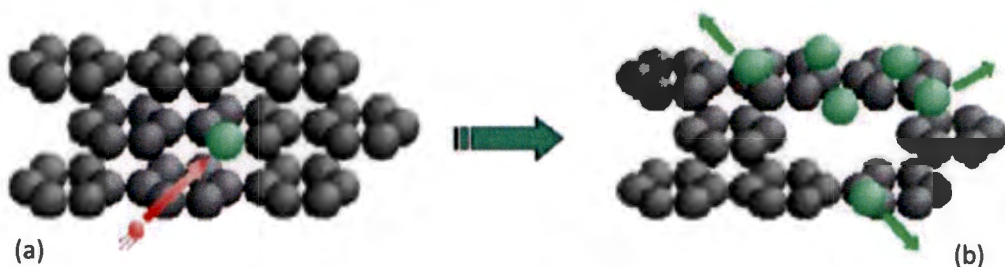
Figure 2.1 The microstructures of new nuclear graphite in the (a) non-irradiated and (b) irradiated states

A new plane forms, and hence expansion along the c-axis occurs (Figure 2.2). The in-plane C-C bond is very strong.
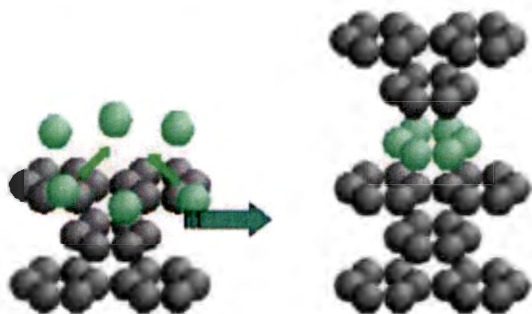
Figure 2.2 New plane forms, c-axis expansion

One of the other advantages of graphite is the porosity of graphite. The pores make it possible to capture the recoil ^{117m}Sn which is the product of interest (Figure.2.3).
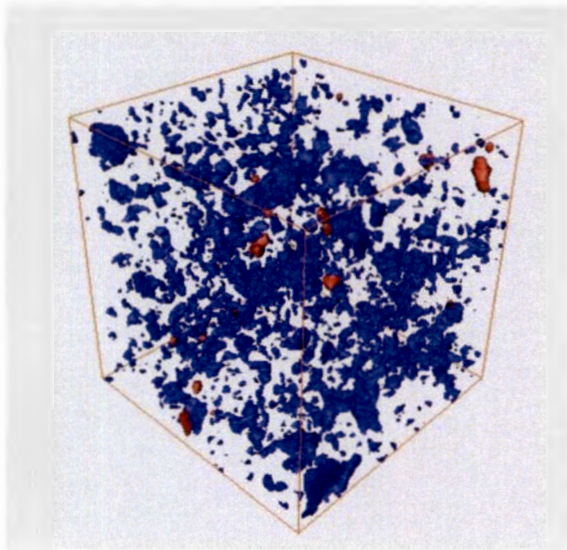
Figure 2.3 3D volume reconstructions of 1 mm^3 BEPO graphite showing porosity (Lensa et al., 2010)

2.11.1 Types of graphite

- Amorphous graphite
- Flake graphite
- Vein graphite

The graphite flakes is one of the recoil capture media that will be used in this study because of the characteristics that it possesses, one being its stability. Graphite is less prone to irradiation damage and resistant against radiolysis.

2.12 Recoil

The recoil process involves the emission of a gamma ray, which removes the nuclear excitation energy; impart recoil energy to the atom to break most chemical bonds (n, γ-recoil). If, after rupture of the bonds, the product atoms exist in a chemical state different and separable from that of the target atoms, the former may be isolated from the large mass of inactive target (Figure 2.5) (Steinebach et al., 2012).
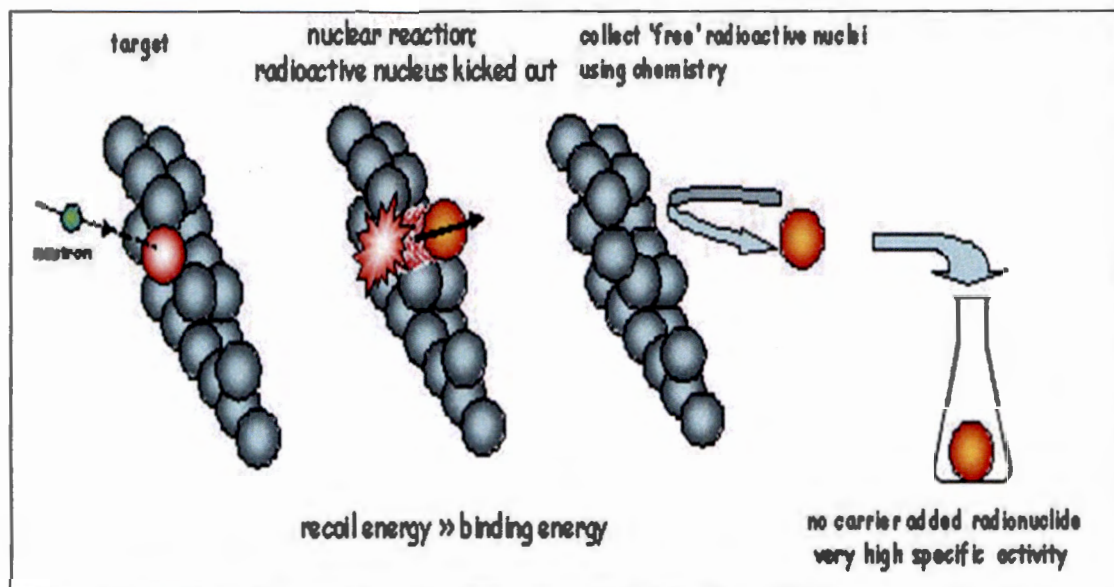
Figure 2.4 Szilard Chalmers reaction (Steinebach et al., 2012).

There are three conditions that have to be met for the Szilard-Chalmers separation to be possible. The radioactive atom in the process of its formation must be loose from its molecule, it must neither recombine with the molecular fragment from which it separated nor rapidly interchange with inactive atoms in other target molecules, and a chemical method for the separation of the target compound from the radioactive material in its new chemical form must be available. Most chemical bond energies are in the range of 1 to 5 eV (20 000 to 100 000 cal per mole) (Friedlander et al., 1981)

The main objective of the Szilard-Chalmers process or reaction is to produce radioisotopes with high specific activity with no carrier added radionuclide. Most medical radioisotopes are produced via neutron capture (n, γ) reactions and all decay by gamma emission, so that the nucleus receives some recoil energy in this process. A γ-ray of energy E_γ, has a momentum $P_\gamma = E_\gamma/c$. To conserve momentum, the recoiling atom must have an identical momentum, and therefore the recoil energy, $R = P_\gamma^2/2M = E_\gamma^2/2M^2c$, where M is the mass of the atom. For M in the atomic mass units and E_γ in millions of electron volts we have

$$R = \frac{537E_\gamma^2}{m} \; eV \qquad\qquad 2.17$$

These atoms are referred to as hot atoms and the field is hot atom chemistry. Hot atom chemistry is the study of the chemical reaction that occurs between high-energy atoms and ions and (usually) thermal energy atoms, molecules, ions, and radicals (Gordus, 1990).

In 1934, Szilard-Chalmers were the first to report a study of hot atom chemistry also known as the chemical effect of nuclear transformation (CENT). Friedlander et al. (1981) irradiated many different organic halides (including CCl_4, $C_2H_4Cl_2$, C_2H_5Br, $C_2H_2Br_2$, C_2H_5Br, CH_3I) and the products of neutron capture reactions ([38]Cl, [80]Br, [82]Br, [128]I) removed by various techniques. More studies have been done on uranium and other fission processes in hot atom chemistry. The hot atom chemistry reactions of fission products, coupled with fast separation techniques including gas chromatography, have also been used to study the properties of fission products (Gordus, 1990).

The recoil method was investigated for separating the produced radioisotope [198]Au. The radioisotope was produced from isotopic ally pure (natural) [197]Au; the target was irradiated in high flux (1 x 10^{14} neutron/cm^{2}s thermal flux) of the reflector of the University of Missouri Research Reactor (Chengy et al., 1999).

2.13 Gamma-ray spectroscopy

Gamma-ray spectroscopy is the quantitative study of the energy spectra of gamma-ray sources, in the nuclear industry, geochemical investigation, and astrophysics. Gamma-ray spectroscopy will be used in this study to determine or measure the activity of the product. Most radioactive sources produce gamma-rays, which are of various energies and intensities (Anusha. et al 2011)

2.13.1 Gamma-ray characteristics

Gamma rays are the highest-energy form of electromagnetic radiation, being physically the same all other forms (e.g. X rays, visible light, infrared, radio) but having higher proton energy due to their shorter wavelength. Because of this, the energy of gamma-ray photons can be resolved individually, and gamma –ray spectrometer can measure and display the energies of the gamma-ray photons detected. (Anusha et al., 2011).

2.13.2 High Purity Germanium (HPGe)

High Purity Germanium (HPGe) is the only radiation detection technology that provides sufficient information to accurately and reliably identify radionuclides from their passive gamma ray emissions (Hossain et al., 2012). HPGe technology, coupled with state-of-the-art real-time spectral analysis algorithms and field proven supporting electronics, can accurately identify and ascertain whether alarms were caused by innocent radiological sources, or if true nuclear or radiological dangers are present (Hossain et al., 2012).
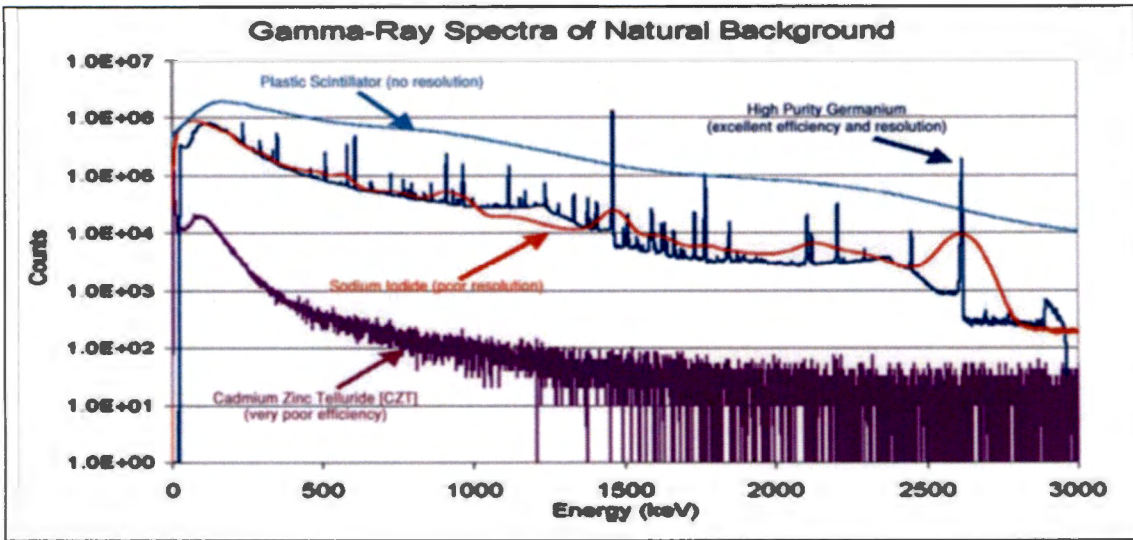
Figure 2.5 Comparison of natural background radiation

(Figure 2.5 compares natural background radiation of four different types of radiation detectors. High Purity Germanium (HPGe) has a high resolution ability. Plastic scintillator detectors have no ability to resolve gamma peaks while sodium iodide (NaI) and cadmium zinc telluride CZT) detectors have limited abilities to resolve the gamma lines.

2.14 Inductively Coupled Plasma

Inductively Coupled Plasma (ICP) is an excellent ion source for inductively coupled plasma mass spectrometry (ICPMS). ICP/OES is a proven commercial success, and the future is still bright for ICP-based spectroscopic techniques (Hou et al., 2000). The analytical advantage of ICP is because it has capability for efficient and reproducible vaporization, atomization, excitation, and ionization for a wide range of elements in various sample matrices.

CHAPTER 3: EXPERIMENTAL METHODS

3. 1 Experimental Reagents

The following reagents were purchased from Sigma-Aldrich: Sulphuric acid (H_2SO_4, F.W. 98.08 g.mol^{-1}, 32% pure, density 1.80 kg/l), hydrochloric acid (HCl, F.W. 36.46 g.mol^{-1}, 32% pure, density = 1.16 kg/l), nitric acid (HNO_3, F.W. 63.01 g.mol^{-1}, 55% pure, density = 1.3 kg/l), sodium hydroxide (NaOH, F.W. 40.00 g.mol^{-1}, 98%), graphite (C, F.W. 12.01 g.mol^{-1}, density = 2.23 g.cm^{-3}), aluminium (Al, F.W. 26.98 g.mol^{-1}, density = 2.7 g.cm^{-3}), and activated carbon (C, F.W. 12.01 g.mol^{-1}, density = 2.1 g.cm^{-3}). Deionised water used in the preparation of solutions was prepared by passing distilled water through a milli-Q-water purification system (Millipore, Bedford, MA, USA).

3.2 Preparation of Mixture of Acids

The mixture of acids was prepared by mixing 18 ml of H_2SO_4 and 6 ml HNO_3. The ratio was selected to be the same as the ratio of nitric and hydrochloric acids in aqua regia. The mixture was able to extract tin when cold experiments were performed.

3.3 Towards the choice of recoil capture media

Aluminium powder, aluminium oxide (Al_2O_3), activated carbon and graphite were selected to determine the choice of recoil capture medium in the cold experiment prior to hot experiments.

Five samples of 0.5 g of graphite each were heated in an oven (120 °C) for a day to dry the powder and cooled for 30 min. Each sample of graphite powder was pressed to make pellets using a hydraulic press (Fig 3.2 and Fig 3.3). Samples of aluminium powder and aluminium oxide (Al_2O_3) were also pressed to make pellets.

3.4 The solubility test of tin oxide, graphite, activated carbon, aluminium and aluminium oxide and cold experiments

Tin oxide pellets were pressed to be used as target material. The discs/pellets pressed from the neat tin oxide were brittle and unable to withstand excessive handling during target preparation, irradiation and processing; therefore aluminium and graphite were added to the oxide to serve as a binder, preventing the fragmentation of the tin oxide target pellets. Table 3.1 shows the tin oxide targets, where (C) and (Al) denote graphite and aluminium binders respectively. The combined mass of the tin oxide and the binder was 0.5 g.

Table 3.1 Targets of tin oxide and recoil capture media for cold experiments

Tin oxide pellets/powder	Recoil capture media	Mass tin oxide pellets/powder (g)	Mass recoil capture media (g)
SnO_2 powder	Aluminium pellet	0.5001	0.5004
SnO_2 powder	Aluminium oxide pellet	0.5004	0.5003
SnO_2 powder	Graphite pellet	0.5002	0.5004
SnO_2 (C) pellet	Aluminium pellet	0.5001	0.5003
SnO_2 (C) pellet	Aluminium oxide pellet	0.5001	0.5004
SnO_2 (C) pellet	Graphite pellet	0.5003	0.5002
SnO_2 (C) pellet	Activated carbon	0.5003	0.5000
SnO_2 (Al) pellet	Aluminium pellet	0.5002	0.5001
SnO_2 (Al) pellet	Aluminium oxide pellet	0.5002	0.5001
SnO_2 (Al) pellet	Graphite pellet	0.5001	0.5004
SnO_2 (Al) pellet	Activated carbon	0.5001	0.5003

Targets were prepared as a sandwich, the tin oxide discs or powder between pellets of the respective recoil capture media (Table 3.1). These sandwiched targets were then folded in aluminium foil and put in a glass (politop) and sealed. A picture demonstrating the prepared target such as a SnO_2 and graphite flake pellet is given in Figure 3.1.
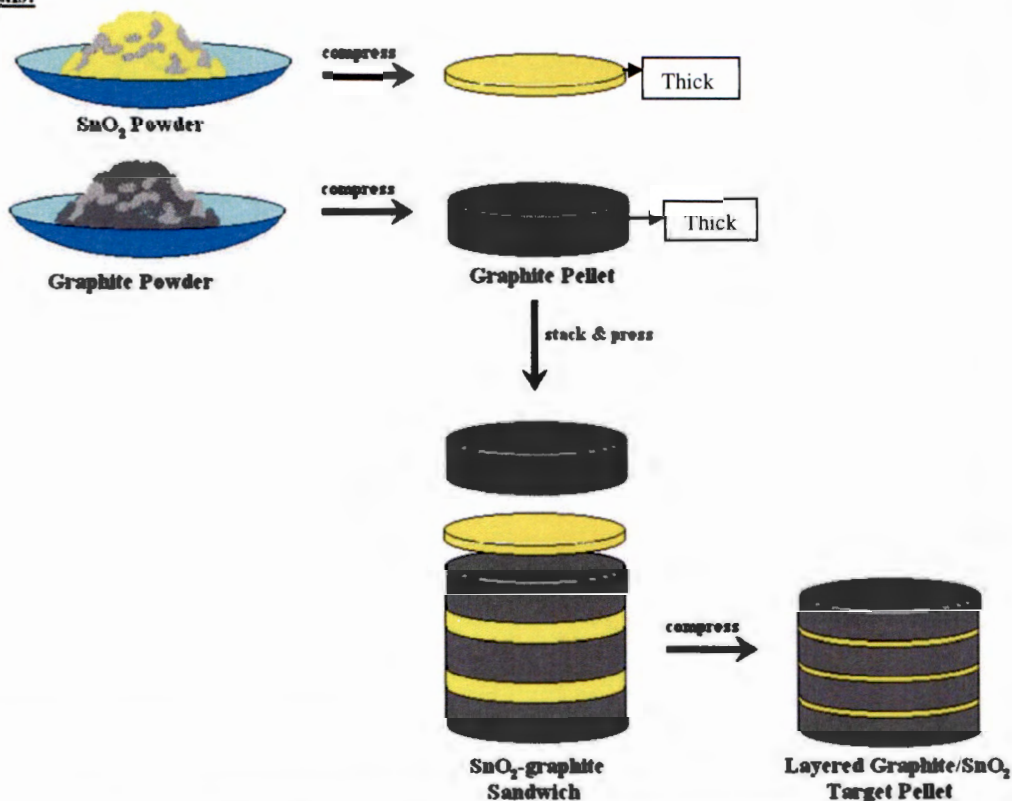
Figure 3.1 Layered graphite/SnO$_2$ pellet target

The mass of the tin oxide powder that was used to prepare tin oxide pellets (Figure 3.1.) was 0.3900 g for each target and that of the recoil capture media graphite and activated carbon were 0.400 g. Aluminum or graphite were used as binding materials and the mass was 0.01 g. The whole target consisted of one pellet of graphite on top and at the bottom and in the middle alternated with tin oxide pellets. Also the targets of tin oxide powder were prepared in the same position.

As a simulation, in preparation for active runs, the targets were opened behind a lead shield and dissolved in a combination of sulphuric acid and nitric acid. One milliliter of each solution was taken for Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analysis at Pelindaba Analytical Lab to determine the total tin concentration. The technique is based upon the spontaneous emission of photons from atoms and ions that have been excited in an RF discharge

3.5 To test the extraction of tin dioxide (SnO$_2$) in various solvents

Tin (IV) oxide (0.500 g) was weighed into each of four different politops and 5 ml of solvent such as hydrochloric acid (HCl), sulphuric acid (H$_2$SO$_4$), nitric acid (HNO$_3$), or sodium hydroxide (NaOH) was added. Tin (IV) oxide (0.0800 g) was weighed into a fifth a politop and 5 ml of mixture of concentrated acids (H$_2$SO$_4$/HNO$_3$) was added.

3.6 Experimental set up for preparation of pellets

The amount of 0.3900 g tin dioxide (SnO$_2$) and 0.01 g of binding material (aluminium or graphite) nanopowder were mixed and weighed into an evacuable pellet die (Figure 3.2). A manual hydraulic press (Figure 3.3) was used to prepare the pellets.

Figure 3.2 Evacuable pellet die

Figure 3.3 Manual Hydraulic Press

3.7 Experimental procedure

3.7.1. Irradiation of targets in the SAFARI-1 reactor

Each target of tin oxide pellets or powder and recoil capture media (as given in Table 3.3), were folded separately in aluminium foil and put in a glass politop and sealed. The targets were irradiated in a hydraulic position for 24 h in the SAFARI-1 reactor at Pelindaba. After irradiation, the targets were left for 24 h to cool down before chemical processing.

Table 3.2. Targets for irradiation

Tin oxide pellets/powder	Recoil capture media	Mass tin oxide pellets/powder (g)	Mass recoil capture media (g)
SnO_2 nanopowder	graphite flake pellet	0.4003	0.802
SnO_2 nanopowder	graphite rod	0.4005	0.072
SnO_2 (C) pellet	graphite flake pellet	0.4056	0.813
SnO_2 (C) pellet	graphite flake	0.4056	0.806
SnO_2 (C) pellet	activated carbon	0.4056	0.806
SnO_2 (Al) pellet	graphite flake pellet	0.4086	0.809
SnO_2 (Al) pellet	graphite flake	0.486	0.809
SnO_2 (Al) pellet	activated carbon	0.4086	0.805

3.7.2. Chemical processing of irradiated targets and activity measurements

The activities of the irradiated targets were measured using a Capintec CRC15 dose calibrator (Fig. 3.4) before they were opened. After the targets were opened behind a lead shield, the tin oxide was separated from the activated carbon or graphite. A mixture of sulphuric and nitric acid (5 ml) was added to the tin (IV) oxide and to the activated carbon or graphite. The solutions were incubated for 12 h to dissolve. The solutions were extracted using a syringe and transferred to centrifuge tubes. The activities of the extracted solutions were measured in

a Capintec CRC15 dose calibrator. The activities of the extracted samples were also measured using γ-spectroscopy (counting for 15 min).

Capintec CRC15 dose calibrator (see Figure 3.4) is the gold standard for dose calibrators in Nuclear Medicine Departments around the world. The LCD shows a large unit of that shows the name, activity (in Ci or Bq) and calibration number. A custom alphanumeric keyboard drives all of the menus and functions.
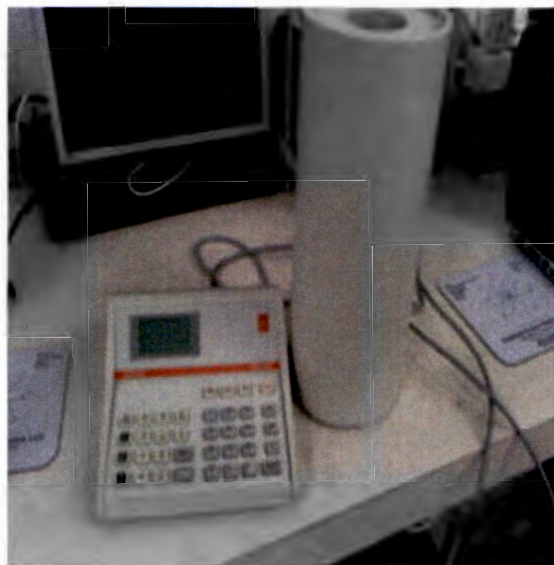
Figure 3.4 Capintec CRC15 dose calibrator

3.7.3 Gamma Spectroscopy

Gamma spectroscopy was used to confirm the ratio of ^{117m}Sn vs ^{113}Sn in the irradiated samples as well as to determine if other isotopes were activated in the process which could impact on the measurements performed by the Capintec dose calibrator.

3.7.4 Genie™ 2000 Gamma Analysis Software

The Genie 2000 Gamma Analysis Software package includes a set of advanced analysis algorithms for further processing of gamma spectra acquired via the Genie 2000 Basic Spectroscopy Software. These algorithms provide a complete analysis of gamma ray spectra obtained from any type of gamma detector. The software is based upon time proven methodologies that have a long history of acceptance and refinements, ground-breaking analysis and calibration techniques.

3.7.5. ICP-OES analysis

Samples of the extracted solutions (1 ml) were diluted with 5 ml of 1.5 M HNO_3 for Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analysis at Pelindaba Analytical Laboratory to determine the total tin concentration.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Materials and target composition

Tin oxide (SnO_2) was used because it is generally chemically inert for post-irradiation extraction (Jansen, 2005). Furthermore, SnO_2 is thermally stable with a melting point of 1127°C. For the same reasons, activated carbon and graphite were used as recoil capture media.

Sulphuric and nitric acid were chosen because cold experiments were performed prior, in order to test extraction of the graphite activated carbon and tin oxide (SnO_2). Also sulphuric and nitric acid are both strong acids and oxidizing agents. Nitric acid does not differ much from sulphuric acid with respect to its physical and chemical properties. Nitric acid is also a strong acid, a powerful oxidizing agent, and it is soluble in water. It reacts with metals and numerous non-metallic substances and compounds and the resultant reactions can be violent. Nitric acid is also used for metal extraction.

The binding materials, namely graphite and aluminum, were chosen because of the physical and chemical properties they possess. Fine graphite powder is used as a moderator. Natural uranium will not undergo nuclear fission by itself because neutrons emitted by [235]U fission tend to be absorbed by [238]U. However, if the emitted neutrons can be slowed down, [238]U is less likely to absorb them, and enough are available to fission [235]U and keep the reaction going. Graphite has the useful property that it can slow neutrons down without absorbing them, so uranium lumps are imbedded in a graphite matrix with appropriate spacing. The neutrons entering the graphite will be slowed down, and when they finally hit a lump of uranium they are likely to be taken up by [235]U and cause fission (Liang, 2012). Under irradiation, graphite undergoes changes in its thermo-mechanical properties, especially via swelling and irradiation-induced creep, which affects the graphite's operational life time.

Aluminium is a lightweight, durable metal. Aluminium was selected as it is routinely used as a component of targets for irradiation and production of radioisotopes.

4.2   Results of cold and hot experiments

Table 4.1 and Table 4.2 list the results of all cold experiments which were conducted prior to active experiments. Cold experiments were conducted, firstly to determine the solvents or acids which can extract/dissolve tin oxide, secondly to determine or select the best recoil capture media, and thirdly to determine the binding materials.

Table 4.1 The extraction of tin dioxide (SnO_2) in various solvents

Name	Solvent (5 ml)	Mass (g)	Temperature (°C)	Observation
Tin oxide (SnO_2)	NaOH	0.4013	100	Tin oxide settled at the bottom with orange solution
Tin oxide (SnO_2)	HCl	0.4014	90	Tin oxide settled at the bottom with yellow solution
Tin oxide (SnO_2)	H_2SO_4	0.4012	110	Tin oxide settled at the bottom but dissolves slightly with white solution
Tin oxide (SnO_2)	HNO_3	0.4013	100	Tin oxide settled at the bottom and dissolves slightly with brown solution

Table 4.2 ICP-OES analysis concentration of tin (Sn)

Name	Mass of SnO_2 weighed for test (g)	Volume of solvent used (ml)	Concentration from ICP analysis (mg/ml)
$SnO_2 + H_2SO_4/HNO_3$	0.4007	5.00	29.0
$SnO_2 + HCl/HNO_3$	0.4006	5.10	333
$SnO_2 + HNO_3$	0.4005	5.40	40.0
$SnO_2 + NaOH$	0.4002	5.30	45.3
$SnO_2 + HCl$	0.4005	5.00	305.0
$SnO_2 + H_2SO_4$	0.4008	5.10	35.5

All the targets listed in Table 3.1 were extracted in various solvents and combination of sulphuric and nitric acid, and it was observed that during incubation neither aluminium nor

aluminium oxide dissolved in the combination of sulphuric acid and nitric acid. However, graphite and activated carbon became suspended or dispersed in the solutions.

The two binding materials, aluminium and graphite, were used because tin oxide on its own did not form robust pellets/discs when pressed in the evacuable pellets dies with a Manual Hydraulic Press (Figure 3.1 and Figure 3.2). The choice of recoil capture media were chosen because of their physical properties and stability. Aluminium oxide was aborted as it damaged the dies, making it difficult to retrieve the pellets after pressing.

The extraction of tin oxide (SnO_2) was tested amongst various solvents and temperature to observe the effect of heat in the extraction of tin oxide and Table 4.1 gives the observations /results and the effect of solvents in tin oxide.

Cold experiments were performed, results and observation are given in Table 4.1, each solvent behaved differently with tin oxide. The objective was to identify a mixture that will not dissolve the SnO_2 target material, but instead preferentially extract the $[^{117m}Sn]$ $Sn(II)$ from the RCM only. If there is dissolution of the SnO_2 target material, it will effectively reduce the specific activity. Therefore, the sulphuric acid and nitric acid mixture was ideal for extraction.

Cold experiments were also performed prior to radioactive experiments to determine the total concentration of natural tin obtained from tin oxide with different solvents and acids by using (ICP-OES) (Inductively Coupled Plasma- Optical Emission Spectroscopy) analysis. The concentration for the targets is given in Table 4.2.

After the tin oxide (SnO_2) was dissolved in various solvents and heated, each solution yielded different concentrations of tin (Sn) and this can be explained by the effect of each acid or solvent.

Eight targets were irradiated in SAFARI-1 and the specific activity and activity of the targets were measured before extraction (Table 4.3).

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Table 4.3 Specific activities of the targets before extraction

Targets	Mass of SnO$_2$ calculated (mg)	Activity of ^{117m}Sn (MBq)	Specific activity of ^{117m}Sn (MBq/mg)
SnO$_2$ nanopowder/graphite flake pellet	306.1	55.10 ± 1.86	0.18 ± 0.006
SnO$_2$ nanopowder/graphite rod	241	4.82 ± 0.71	0.015 ± 0.003
SnO$_2$ pellet (C)/graphite flake pellet	311	52.90 ± 13.68	0.17 ± 0.043
SnO$_2$ pellet (C)/graphite flake	320	57.59 ± 9.16	0.18 ± 0.028
SnO$_2$ pellet (C)/activated carbon	320	32.00 ± 20.67	0.10 ± 0.064
SnO$_2$ pellet (Al)/graphite flake pellet	311	59.10 ± 22.50	0.19 ± 0.072
SnO$_2$ pellet (Al)/graphite flake	318	63.60 ± 17.38	0.20 ± 0.054
SnO$_2$ pellet (Al)/ativated carbon	314	72.30 ± 36.84	0.23 ± 0.117

*Mass of tin 315.1 mg (total mass of tin calculated from the mass SnO$_2$). ^{117m}Sn activity was decay corrected to end of irradiation.

The specific activities of targets before opening are given in Table 4.3. Here it was assumed that the ^{117m}Sn activity was due to SnO_2 as a whole. The activities were measured using a Capintec dose calibrator, and were used as a reference specific activity before extraction. The target that showed the highest specific activity (Table 4.3) was that of the compressed tin oxide pellet comprising of aluminium as a binding material, and activated carbon as recoil capture medium. The target with the lowest specific activity was that prepared with tin oxide nanopowder and graphite rod as a recoil capture medium.

The specific activities of most of the targets fell within the same range, taking into account the standard errors (Figure 4.1). Statistically, there is no significant difference between the targets (see Appendix A).
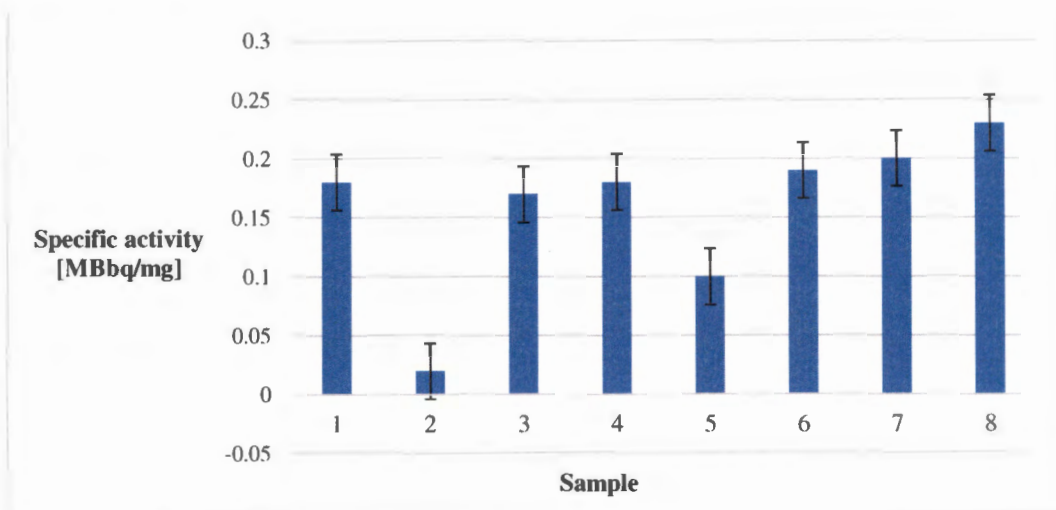
1- SnO_2 nanopowder - Graphite flake pellet; 2- SnO_2 nanopowder - Graphite rod; 3- SnO_2 pellet (C) - Graphite flake pellet; 4- SnO_2 pellet (C) – Graphite flake; 5- SnO_2 pellet (C) - Activated carbon; 6- SnO_2 pellet (Al) - Graphite flake pellet, 7- SnO_2 pellet (Al) - Graphite flake; 8- SnO_2 pellet (Al) - Activated carbon

Figure 4.1 Specific activities of ^{117m}Sn targets before extraction.

4.3 Discussion

After physical separation of the recoil capture media and the tin oxide components of the target the specific activities of ^{117m}Sn in each of these were determined after extraction with a combination of sulphuric acid and nitric acid (Table 4.4). The mass of the extracted tin was determined by ICP-OES and γ-spectroscopy was used to measure the ^{117m}Sn activity after incubation overnight in a combination of sulphuric acid and nitric acid and subsequent filtration.

Table 4.4 Post-extraction specific activities of ^{117m}Sn from tin oxide and recoil capture media components and ICP mass of total tin of the targets

Target		Mass (mg)		Activity(MBq)		Specific activity (MBq/mg)	
SnO₂	Recoil capture medium	SnO₂	Recoil capture medium	SnO₂	Recoil capture medium	SnO₂	Recoil capture medium
Nanopowder	Graphite flake pellet	0.63 ± 0.73	0.025 ± 0.00	1.53 ± 1.61	9.69×10^{-4} ± 0.001	2.42 ± 1.05	0.03 ± 0.049
Nanopowder	Graphite rod	0.19 ± 0.09	0.30 ± 0.10	0.03 ± 0.03	4.85×10^{-3} ± 0.004	0.16 ± 0.11	0.016 ± 0.165
*Carbon pellet	Graphite flake pellet	4.43 ± 2.23	0.09 ± 0.09	0.88 ± 0.65	0.02 ± 0.027	0.20 ± 0.13	0.22 ± 0.135
*Carbon pellet	Graphite flake	0.84 ± 0.49	0.26 ± 0.41	0.17 ± 0.09	0.06 ± 0.104	0.20 ± 0.04	0.23 ± 0.128
*Carbon pellet	Activated carbon	0.30 ± 0.02	0.24 ± 0.09	0.15 ± 0.21	0.02 ± 0.024	0.50 ± 0.67	0.08 ± 0.141
#Aluminium pellet	Graphite flake pellet	1.36 ± 0.45	0.98 ± 0.78	0.33 ± 0.06	0.23 ± 0.199	0.24 ± 0.13	0.23 ± 0.164
#Aluminium pellet	Graphite flake	0.54 ± 0.43	0.49 ± 0.40	0.09 ± 0.09	0.16 ± 0.218	0.17 ± 0.06	0.33 ± 0.325
#Aluminium pellet	Activated carbon	1.07 ± 0.12	0.23 ± 0.20	0.18 ± 0.03	0.02 ± 0.008	0.17 ± 0.01	0.09 ± 0.153

* Refers to the graphite binding material used to prepare the SnO₂ target pellet. # refers to the aluminium binding material used to prepare the SnO₂ target pellet.

The target comprising of SnO_2 nanopowder and graphite flake pellets showed a higher specific activity in the SnO_2 component as compared to the rest, whilst the graphite from the same target has the lowest specific activity of all. Considering only the SnO_2 extract, the lowest specific activity was found in the sample of SnO_2 nanopowder with a graphite rod as target. This is consistent with the pre-extracted values (Table 4.3). This can be due to the poor contact surface area between the tin oxide nanopowder and the graphite rod. Furthermore, the low contact surface area would imply a decrease in the moderation of neutrons by the graphite, which means a reduced reactivity and in turn less ^{117m}Sn. The detection limit for the ICP-OES analysis was 0.025 mg. The low activities observed correspond with a low mass that is less than the detection limit for the respective targets. This may have been due to possible inhomogeneity of the samples, which could have arisen from precipitation of tin during a delay between the time of extraction and analysis. In such instances the specific activity of the product may well have been higher.

There may be an additional effect of recoil stabilization that could result in the specific activity of the two components within the same target being the same, or even that the SnO_2 extract possess a higher specific activity than its graphite/carbon counterpart. An example of the latter is the target containing SnO_2 nanopowder and graphite flake pellets. The recoil capture medium acts merely as a stabilizer, where the recoil capture media aid in maintaining the oxidation or ionic state of the recoiled ^{117m}Sn atoms thus preventing them from reverting back to its original SnO_2 form. The same effect could be caused by the binding material being of similar nature as the recoil capture media.

Large errors are mainly due to challenges with ICP measurements and the delay between processing and performing the total elemental analysis of the samples, which may have resulted in inhomogeneous samples at the time of measurement. An example of such delays was because of radiological safety considerations, where samples had to be cooled prior to being transferred to the ICP analytical laboratories. Furthermore, the option of diluting the samples to achieve appropriate dose levels introduced additional complications such as hydrolysis of the $[^{117m}Sn]$ Sn(II), which too compromised the homogeneity of the samples. The problem was not so big for the gamma-spectrometry measurements since it is a very robust analytical method.
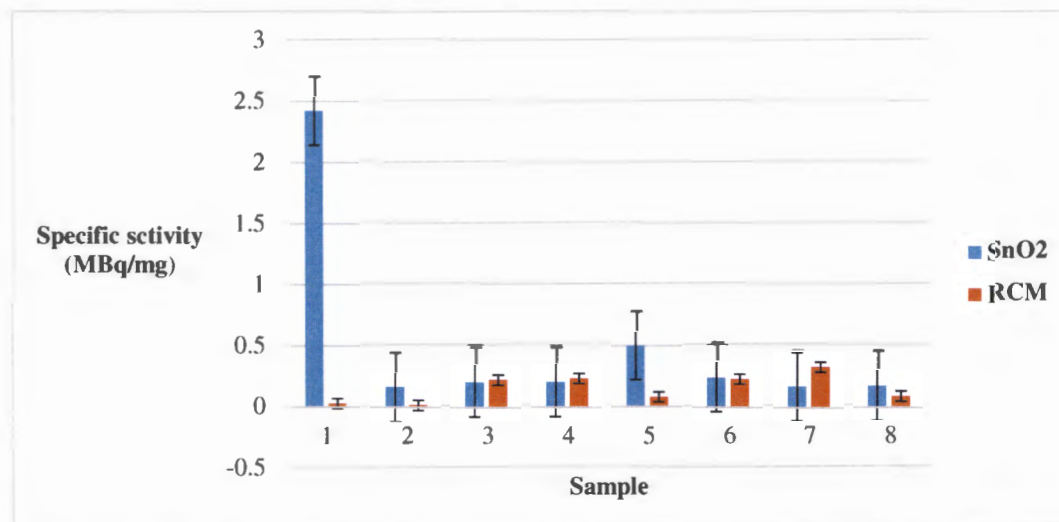
47

1- SnO$_2$ nanopowder - Graphite flake pellet; 2- SnO$_2$ nanopowder - Graphite rod; 3- SnO$_2$ pellet (C) - Graphite flake pellet; 4- SnO$_2$ pellet (C) – Graphite flake; 5- SnO$_2$ pellet (C) - Activated carbon; 6- SnO$_2$ pellet (Al) - Graphite flake pellet,; 7- SnO$_2$ pellet (Al) - Graphite flake; 8- SnO$_2$ pellet (Al) - Activated carbon

Figure 4.2 Specific activity of ^{117m}Sn from tin oxide (in blue) and recoil capture media component (orange) of the targets after opening, physical separation of tin oxide from recoil capture media and extraction process.

All targets were grouped according to their recoil capture media and the averages of the specific activities from the SnO$_2$ and recoil capture media were compared (Table 4.5) in order to identify the better of the recoil capture media or stabilizers. Graphite flake pellet and graphite flake samples gave higher specific activities after processing.

Table 4.5 Comparison of the specific activities of the ^{117m}Sn obtained for the different types of recoil capture media, as extracted from the recoil capture medium itself and SnO$_2$ component.

Recoil capture medium	Specific activity	
	Tin oxide (MBq/mg)	Recoil capture medium (kBq/mg)
Graphite flake pellets	0.95 ± 1.27	0.16 ± 0.12
Graphite flake	0.19 ± 0.02	0.28 ± 0.01
Graphite rod	0.16 ± 0.40	0.016 ± 0.165
Activated carbon	0.34 ± 0.23	0.085 ± 0.226

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The effect of the binding material was also considered. The targets prepared and the binding materials used are given in Table 4.6. A target prepared without the binder is included to compare the effect of the binding material on the specific activity of ^{117m}Sn. The aluminium binder proved better for the extracts from the recoil capture media. However, the specific activity obtained from the SnO_2 component was better in the absence of the binding materials (Table 4.6).

Table 4.6 Specific activity of targets prepared from binding materials after extraction process of the recoil capture media samples and tin oxide components

Binding material	Specific activity	
	Tin oxide (MBq/mg)	Recoil capture medium (kBq/mg)
Aluminium	0.19 ± 0.04	0.21 ± 0.13
Graphite fine powder (C)	0.30 ± 0.17	0.18 ± 0.10
Tin oxide nanopowder only (not compressed)	1.29 ± 1.60	-

4.3 Gamma Spectroscopy

A number of gamma spectra acquired from different targets irradiated are presented in Figure 4.3 to Figure 4.6. The gamma emission lines for ^{113}Sn (392 keV 64%) and ^{117m}Sn (159 keV, 86%) are clearly visible in all the graphs. No major other peaks were recorded that would not influence the overall measurements in the experiments when carbon or graphite was mixed with the SnO_2 neither where Al was added to the target.
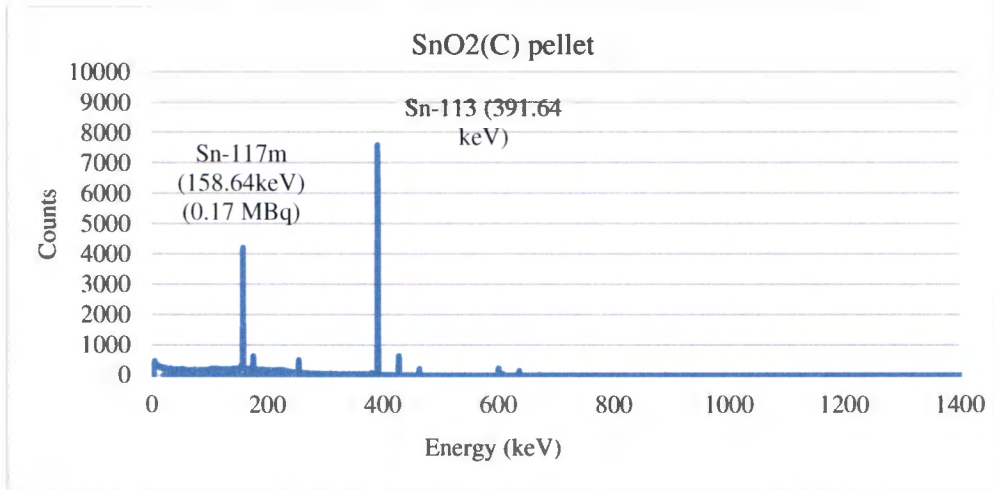
Figure 4.3 γ-Spectrum of ^{117m}Sn in tin oxide with 0.01 g graphite as binding material
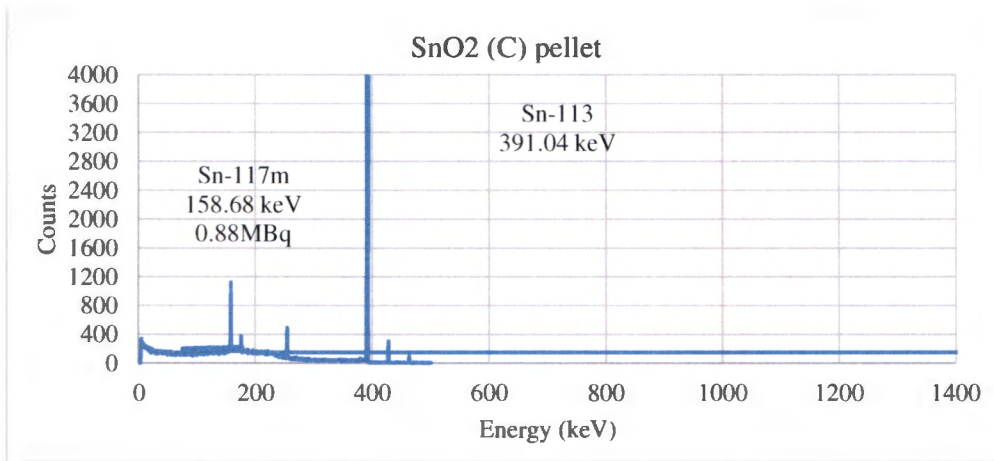
Figure 4.4 γ-Spectrum of ^{117m}Sn in tin oxide pellet with 0.01 g graphite as binding material
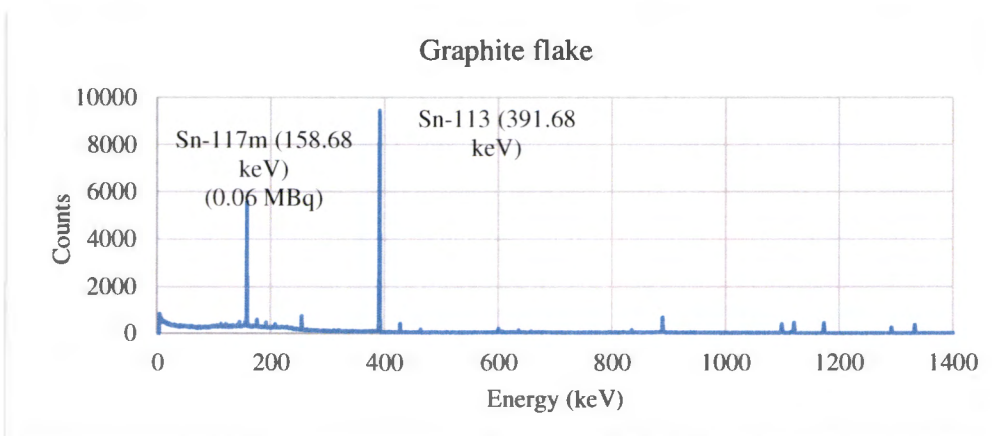
Figure 4.5 γ-Spectrum of ^{117m}Sn in recoil capture medium of graphite flake
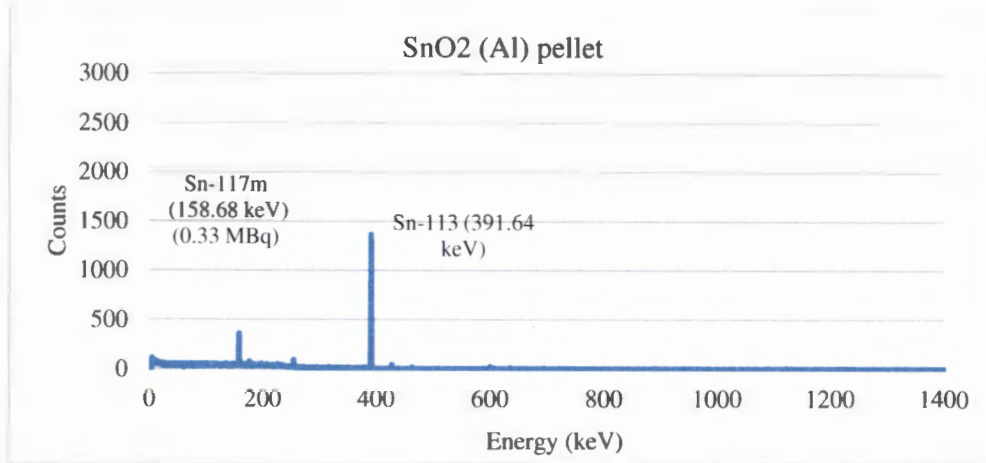
Figure 4.6 γ-Spectrum of ^{117m}Sn in tin oxide with 0.01g aluminum as binding material

4.4 Enrichment factor

The enrichment factor is defined as the ratio of the relative frequency of a certain isotope in an isotope mixture to the relative frequency of this isotope in the natural isotope mixture. The enrichment factors of the extracted activities for the recoil capture media and SnO_2 (Table 4.4) were calculated against the specific activities of the targets prior to processing (Table 4.3). The enrichment factor was determined using Equation 4.1.

$$EF = \frac{SA_{post-extraction}}{SA_{pre-extraction}}$$

4.1

Where EF is the enrichment factor and SA is the specific activity (Bq/mg).

Based on the results obtained in this study (Tables 4.7), it cannot be concluded as to any enrichment obtained due to recoil per se. There was no statistically significant difference between the enrichment factors obtained for the various targets. The enrichment of SnO_2 exceeds that of their respective recoil capture media values, which could be due to a possible recoil stabilization effect brought about by the recoil capture media.

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Table 4.7 Enrichment factor of ^{117m}Sn from tin oxide and recoil capture media calculated from the specific activity of the tin oxide after the extraction process to pre-extraction of the samples

SnO$_2$	Recoil capture medium	Enrichment factor	
		From tin oxide	From recoil capture medium
Nanopowder	Graphite flake pellet	13.44 ± 24.32	0.16 ± 0.59
Nanopowder	Graphite rod	8.00 ± 3.43	0.80 ± 1.07
Carbon pellet	Graphite flake pellet	1.18 ± 0.75	1.41 ± 0.73
Carbon pellet	Graphite flake	1.11 ± 0.28	1.29 ± 0.67
Carbon pellet	Activated carbon	5.00 ± 3.38	0.80 ± 1.77
Aluminium pellet	Graphite flake pellet	1.20 ± 0.72	1.21 ± 0.87
Aluminium pellet	Graphite flake	0.85 ± 0.42	1.65 ± 0.40
Aluminium pellet	Activated carbon	0.74 ± 0.45	0.39 ± 1.21
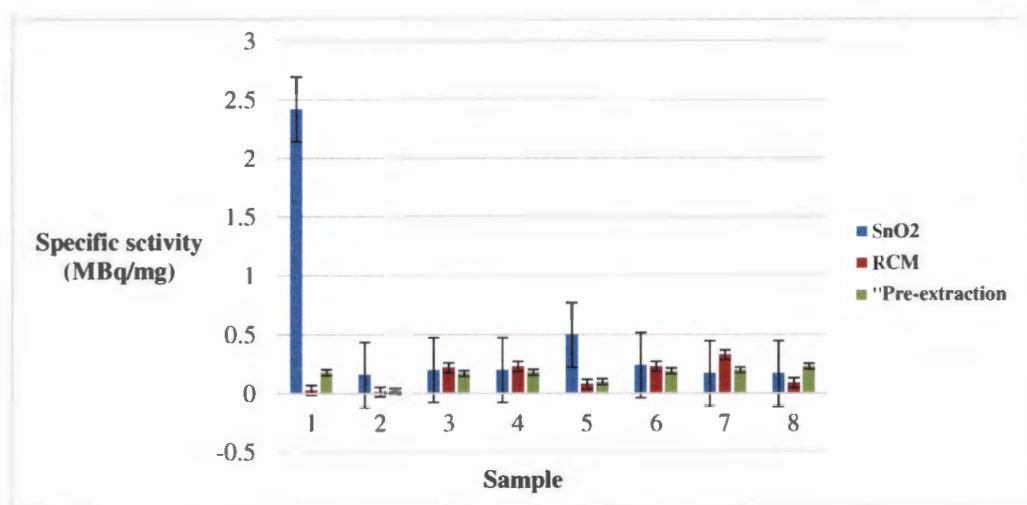
1- SnO$_2$ nanopowder - Graphite flake pellet; 2- SnO$_2$ nanopowder - Graphite rod; 3- SnO$_2$ pellet (C) - Graphite flake pellet; 4- SnO$_2$ pellet (C) – Graphite flake; 5- SnO$_2$ pellet (C) - Activated carbon; 6- SnO$_2$ pellet (Al) - Graphite flake pellet;   7- SnO$_2$ pellet (Al) - Graphite flake; 8- SnO$_2$ pellet (Al) - Activated carbon

Figure 4.7 Specific activity of ^{117m}Sn from pre-extraction targets to post-extraction of tin oxide and recoil capture media components.

During the nuclear reaction, the recoiled atoms undergo a change in oxidation state. The presence of the graphite and carbon (in combination with their respective binding material) may have aided in preventing the recoiled ^{117m}Sn atoms from reverting back to their original form, thus making it possible to separate the activity from the SnO_2 target materials.

CHAPTER 5: CONCLUSION AND FUTURE WORK

5. 1 Conclusion

The aim of the experiments was to produce ^{117m}Sn with a high specific activity using trhe Szilard-Chalmers reaction. After reaching all the objectives of the study and performing the experimental method of the study, it was discovered that even though there was no significant sign of enrichment, where the enrichment factor is defined as the ratio of the relative frequency of a certain isotope in an isotope mixture to the relative frequency of this isotope in the natural isotope mixture, this set of experiments demonstrated the possibility that the recoil atoms can be stabilized upon ejection from the target lattice thus preventing them from reverting back to their original form.

Graphite and activated carbon were considered as effective recoil capture media due to their chemical inertness towards strong acids and alkalis during post bombardment extraction of the ^{117m}Sn atoms/ions and their robustness against radiation damage when exposed to severe neutron fluxes for prolonged periods. The use of graphite and activated carbon as recoil capture media added no or little benefit since the oxide on its own yielded the same enrichment factors. The most important aspects when considering the use of any recoil capture medium remains the effective separation from the target material and the extraction of the embedded recoil activity.

The method that was used to produce ^{117m}Sn was adopted for its simplicity for upscaling and implementation for production. Although the effective separation and extraction was not demonstrated, carbon and its allotropes could still well be used as a medium for stabilizing the recoil. What was achieved was the stability of the recoil atom/ions from the neutron capture reaction. Optimization of target design and experimental methodology is needed by examining: (1) the grain size to increase the surface area for effective neutron activation, (2) the ratios between the oxide and the recoil capture media to ensure sufficient contact for recoil capture, (3) the reactor neutron flux and irradiation period, and (4) extraction media and conditions such as pH.

5.2 Future work

- Future work will be to optimise the conditions using tin oxide (SnO_2) nanopowder with graphite flake pellets to further investigate the recoil stabilization effect with the aim of eventually achieving higher specific activities.

- The extraction process will be modified by using an incubator for less exposure to radiation and to prevent loss of activity by using syringes and needles.

- Also by utilising different combinations of concentrated acids for extraction.

- By repeating the combination of tin oxide (SnO_2) pellets with graphite flakes and using different types of binder materials such as aluminium (Al) and graphite powder (C).

- This project will take another few months, and if possibly another Masters or PhD or publication if it actually works.

- This study replaces the acids that have been attempted, with solutions comprising of ligands that is knows to bind selectively with Sn(II). Therefore, classical mineral extraction (much like that of dmgH2 and Ni, but the inverse) will be done. These ligands will be conditioned according to findings of potentiometric data that is already known for Sn(II) and Sn(IV), and could be HEDP, PEIMP or any amino acid (Zeevaart et al., 2004, Jansen et al., 2009)

- Conditions that favours only Sn(II) complexation will be selected, leaving Sn(IV) in solution or as SnO_2 and a Sn(IV) hydroxide precipitate. A whole range of ligands, based on previous potentiometric findings can be tested, providing some scientific rationale to the approach. Furthermore, this can be extended to other nuclides as well.

- An ICP component can be included in the study to test the presence of different metal complexes in the extract. The concept or principle can be similar to the way in which generators work, and maybe in future it won't need much post-irradiation manipulation, but instead the end-user might perform the extraction directly from the appropriately packaged target.

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Appendix A

Statistical analysis

The F-test was determined by using Equation 4.8 for all statistics tables. Table of critical values of F at the $p = 0.05$ level of significance was used to determine the critical value of each table. The critical value of F is 6.94 ($F_{critical}$ (2, 4)). If calculated F-ratio is smaller than the critical value; it can be concluded that the determined F-ratio is likely to occur by chance with $p < 0.05$.

$$f = \frac{\dfrac{n_1(x_1 - \bar{x}) + n_2(x_2 - \bar{x}) + \cdots + n_n(x_n - \bar{x})}{I - 1}}{\dfrac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2 + \cdots + (n_n - 1)s_n^2}{N - 1}} \qquad 5.1$$

Tables A-1 to A-8 serve to identify whether the targets are statically similar according to their composition. Here the effects of the binding materials, aluminium and graphite, were compared in the case of the SnO_2 component (A-7) and for the recoil capture media (Table A-8). The influence of the recoil capture media was tested in tin component for the three configurations of the SnO_2, i.e. with aluminium binder (A-7), graphite binder (A-4) and, nanopowder only (A-5). Similarly, the effect of the recoil capture media were compared in the respective capture media component for the SnO_2 configurations mentioned above (Tables A-5-A-7).

A-1 F-test for tin oxide of SnO_2 (Al), i.e. targets where Al was used as binder for SnO_2 disc.

Name	Mean	Standard deviation	Sample number
Graphite flake pellet	2.42E+5	1.31E+5	2
Graphite flake	1.67E+5	5.91E+4	3
Activated carbon	1.70E+5	8.95E+3	2

$$f = 3.23\text{E-}6$$

A-2 F-test for tin oxide of SnO_2 (C), i.e. targets where graphite was used as a binder for SnO_2 discs.

Name	Mean	Standard deviation	Sample number
Graphite flake pellet	1.99×10^5	1.30×10^5	2
Graphite flake	1.99×10^5	4.09×10^4	3
Activated carbon	4.98×10^5	6.73×10^5	2

$$f = 6.46 \times 10^{-7}$$

The critical value of F is 6.94 ($F_{critical}$ (2, 4)). The calculated F-ratio is smaller than the critical value; it can conclude that the determined F-ratio is likely to occur by chance with $p < 0.05$.

A-3 F-test for nanopowder of SnO_2 for the respective recoil captures media used.

Name	Mean	Standard deviation	Sample number
Graphite flake pellet	2.42×10^6	1.60×10^7	2
Graphite rod	1.61×10^5	1.09×10^5	3

$$f = 1.70 \times 10^{-8}$$

The critical value of F is 10.13 ($F_{critical}$ (1, 3)). The calculated F-ratio is smaller than the critical value; it can conclude that the determined F-ratio is likely to occur by chance with $p < 0.05$.

A-4 F-test for targets containing SnO_2 nanopowder only of recoil capture media

Name	Mean	Standard deviation	Sample number
Graphite flake pellet	3.88×10^4	4.92×10^4	2
Graphite rod	1.94×10^6	1.65×10^5	3

$$f = 6.71 \times 10^{-5}$$

The critical value of F is 10.13 ($F_{critical}$ (1, 3)). The calculated F-ratio is smaller than the critical value; it can conclude that the determined F-ratio is likely to occur by chance with $p < 0.05$.

A-5 F-test for recoil capture media of SnO_2 (Al) targets.

Name	Mean	Standard deviation	Sample number
Graphite flake pellet	2.31×10^5	1.65×10^5	3
Graphite flake	3.24×10^5	3.26×10^5	3
Activated carbon	6.56×10^4	1.54×10^5	2

$$f = 1.69 \times 10^{-6}$$

The critical value of F is 5.79 ($F_{critical}$ (2, 5)). The calculated F-ratio is smaller than the critical value; it can conclude that the determined F-ratio is likely to occur by chance with $p < 0.05$.

A-6 F-test for recoil captures media of SnO_2 (C) containing targets.

Name	Mean	Standard deviation	Sample number
Graphite flake pellet	2.43×10^5	1.36×10^5	2
Graphite flake	2.30×10^5	1.28×10^5	3
Activated carbon	7.49×10^5	1.42×10^5	2

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$$f = 1.88 \times 10^{-6}$$

The critical value of F is 6.94 ($F_{critical}$ (2, 4)). The calculated F-ratio is smaller than the critical value; it can conclude that the determined F-ratio is likely to occur by chance with $p < 0.05$.

Table A-5 to A-8 combines specific activities of the recoil capture media and tin oxide components and evaluate the effects of the recoil capture media on their combined full targets. Example A-3 represents tin oxide components which graphite is a binder and A-7 shows the recoil capture media for the same targets. These were averaged and combined in table A-3. Similarly to tables A-1 and A-8 and tables A-5 and A-7 for tablesA-3 and A-5 respectively.

A-7 F-test SnO_2 (C)

Name	Mean	Standard deviation	Sample number
Graphite flake pellet	$2.21 \times 10^{+5}$	$1.33 \times 10^{+5}$	2
Graphite flake	$2.14 \times 10^{+5}$	$8.45 \times 10^{+5}$	2
Activated carbon	$2.86 \times 10^{+5}$	$4.08 \times 10^{+5}$	2

$$f = 2.6 \times 10^{-8}$$

The critical value of F is 9.55 ($F_{critical}$ (2, 3)). The calculated F-ratio is smaller than the critical value; it can conclude that the determined F-ratio is likely to occur by chance with $p < 0.05$.

A-8 F-test SnO_2 (Al)

Name	Mean	Standard deviation	Sample number
Graphite flake pellet	$2.37 \times 10^{+5}$	$1.48 \times 10^{+5}$	2
Graphite flake	$2.46 \times 10^{+5}$	$1.92 \times 10^{+5}$	2
Activated carbon	$1.18 \times 10^{+5}$	$8.15 \times 10^{+5}$	2

$$f = 7.6 \times 10^{-8}$$

The critical value of F is 9.55 ($F_{critical}$ (2, 3)). The calculated F-ratio is smaller than the critical value; it can conclude that the determined F-ratio is likely to occur by chance with $p < 0.05$.