Deuteron irradiation of W and WO₃ for production of high specific activity ¹⁸⁶Re: Challenges associated with thick target preparation

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ABSTRACT

This investigation evaluated target fabrication and beam parameters for scale-up production of high specific activity ¹⁸⁶Re using deuteron irradiation of enriched ¹⁸⁶W via the ¹⁸⁶W(*d*,2n)¹⁸⁶Re reaction. Thick W and WO₃ targets were prepared, characterized and evaluated in deuteron irradiations. Full-thickness targets, as determined using SRIM, were prepared by uniaxially pressing powdered natural abundance W and WO₃, or 96.86% enriched ¹⁸⁶W, into Al target supports. Alternatively, thick targets were prepared by pressing ¹⁸⁶W between two layers of graphite powder or by placing pre-sintered (1105°C, 12 hours) natural abundance WO₃ pellets into an Al target support. Assessments of structural integrity were made on each target prepared. Prior to irradiation, material composition analyses were conducted using SEM, XRD, and Raman spectroscopy. Within a minimum of 24 hours post irradiation, gamma-ray spectroscopy was performed on all targets to assess production yields and radionuclidic byproducts. Problems were encountered with the structural integrity of some pressed W and WO₃ pellets before and during irradiation, and target material characterization results could be correlated with the structural integrity of the pressed target pellets. Under the conditions studied, the findings suggest that all WO₃ targets prepared and studied were unacceptable. By contrast, ¹⁸⁶W metal was found to be a viable target material for ¹⁸⁶Re production. Thick targets prepared with powdered ¹⁸⁶W pressed between layers of graphite provided a particularly robust target configuration.

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1. Introduction

The potential for application of a therapeutic radionuclide generally stems from several characteristics, including availability, method of production, achievable specific activity, and decay properties (e.g. half-life and characteristics of particulate and photon emissions). Particularly useful radionuclides provide an imageable photon as well as particulate emissions for therapy. Such dual-emission radionuclides are considered theranostic radionuclides (also termed theragnostic) (Baum and Kulkarni, 2012; Srivastava, 2012). Theranostic radionuclides can be incorporated into radiopharmaceuticals to provide the ability to obtain both diagnostic information (e.g. tumor targeting, tissue dose estimates) and effective therapy from the same agent. Two rhenium radionuclides, ^{186}Re ($t_{1/2} = 89.2$ h) and ^{188}Re ($t_{1/2} = 17.0$ h) have theranostic decay properties that make them very attractive for use in targeted radionuclide therapy of cancer. While both radioisotopes of Re can be used for targeted radionuclide therapy, there are some important differences between them. Rhenium-188 has been studied for a variety of radiotherapeutic applications (Knapp Jr, 1998; Knapp Jr et al., 1996; Knapp Jr et al., 1994). It decays by the emission of high-energy β^- particles ($E_{\beta^- \text{ endpoint}} = 2.12$ MeV) and an imageable photon at 155 keV (15.6%) (Knapp Jr, 1998). This radionuclide is produced in a no-carrier-added form (i.e. high specific activity) by β^- decay of ^{188}W ($t_{1/2} = 69.78$ d), and is available from the U.S. Department of Energy as a $^{188}\text{W}/^{188}\text{Re}$ generator (Dadachov et al., 2002; Knapp Jr, 1998; Knapp Jr et al., 1996; Knapp Jr et al., 1994). Unfortunately, the parent for the generator, ^{188}W , is produced by a double neutron capture on enriched ^{186}W target material in a high-flux nuclear reactor (Boschi et al., 2014), potentially limiting its wide-spread application. Further, the high β^- endpoint energy and short half-life of ^{188}Re limits the range of potential applications (Dadachov et al., 2002). Rhenium-186, on the other hand, appears to have a greater potential for development of theranostic radiopharmaceuticals because of its emission of medium-energy β^- particles ($E_{\beta^- \text{ endpoint}}: 1.07 \text{ \& } 0.93$ MeV), which can be used to treat a range of tumor sizes, and its imageable photon emission at 137 keV (9.5%). It is important to note that the emitted photon energy of ^{186}Re is remarkably similar to the 141 keV γ photon of the most widely used diagnostic radionuclide, technetium-99m ($^{99\text{m}}\text{Tc}$). This photon emission is readily compatible with current planar and SPECT/CT imaging equipment available in Nuclear Medicine facilities worldwide. Additionally, the longer 3.7-day half-life of ^{186}Re allows sufficient time for the synthesis and shipment of radiopharmaceuticals, and potentially makes it applicable to a wider range of therapy applications than ^{188}Re .

The principal drawback of ^{186}Re for radioimmunotherapy or targeted radionuclide therapy has been the low specific activity obtained from the traditional nuclear reactor-based (n, γ) production methods (Knapp et al., 1996). Despite high thermal and epithermal neutron cross-sections of ^{185}Re (106 b and 1632 b, respectively), research reactors are only capable of producing specific activities that are considered marginal at best for radioimmunotherapy (Moustapha et al., 2006). Up to 20 Ci of ^{186}Re have been produced with a specific activity at time of processing of ~ 111 GBq/mg (~ 3 Ci/mg) using neutron activation, but this represents only 2% activation to ^{186}Re leaving 98% of the enriched ^{185}Re to compete in the labeling process (Ehrhardt et al., 1997). This specific activity is a major problem for directly labeled antibodies, but is even more of a problem if used in pretargeting protocols (Green et al., 2014; Pagel et al., 2009a; Pagel et al., 2009b). Therefore, methods of obtaining high specific activity ^{186}Re are being sought.

An alternative to neutron activation for production of ^{186}Re is the use of accelerator produced charged particle reactions. These reactions result in much higher specific activities, as the ^{186}Re is produced from a different element that can be chemically separated post-irradiation. Previously published investigations of high specific activity ^{186}Re production have utilized the $^{186}\text{W}(p,n)^{186}\text{Re}$ or $^{186}\text{W}(d,2n)^{186}\text{Re}$ reactions (Alekseev and Lazarev, 2006; Bonardi et al., 2010; Fassbender et al., 2013; Shigeta et al., 1996; Zhang et al., 2001; Zhang et al., 1999). It was concluded from those investigations that activation of ^{186}W by deuterons was preferred over protons as: (1) production yields are at least three time higher (Zhang et al., 2001), (2) the ^{186}Re radionuclidic purity is higher and remains higher (Alekseev and Lazarev, 2006; Zhu et al., 1997), and (3) lower quantities of enriched ^{186}W material are required for the irradiations. This latter point is important as it results in lower costs and facilitates chemical isolation of ^{186}Re from the target material (Bonardi et al., 2010).

The overall goal of this investigation was to demonstrate that production-levels of high specific activity ^{186}Re can be obtained via the ($d,2n$) reaction using thick W targets. Prior reported studies have used a variety of target materials for production of ^{186}Re , including W metal (Bonardi et al., 2010; Zhang et al., 2001; Zhang et al., 1999), WO_3 (Fassbender et al., 2013; Moustapha et al., 2006; Shigeta et al., 1996), $\text{Al}_2(\text{WO}_4)_3$ (Zhu et al., 1997), and W carbides (Richards et al., 2015). However, those studies were limited to “thin” target bombardments or thick target investigations using only natural abundance target

material. Initial assessment of potential target materials for this investigation eliminated $\text{Al}_2(\text{WO}_4)_3$ as a target material due to the production of ^{24}Na in deuteron irradiations of aluminum (Wilson et al., 1976). While the half-life of ^{24}Na is only 15 hours, its high-energy gamma emissions (including 1369 keV & 2754 keV) are present in nearly 100% abundance, resulting in difficulties with handling, transfer and storage. Tungsten metal is the obvious choice for a target material due to its higher density, higher thermal conductivity and higher melting point. In fact, comparisons of W metal and WO_3 as target materials have shown that W metal provides higher ^{186}Re yields (based on atomic ratios). However, it is important to also consider losses occurring in the isolation process and recovery of enriched W metal. Radiorhenium has been previously shown to be chemically separable from matrices of WO_3 via dry distillation (Lapi et al., 2007; Novgorodov et al., 2000), liquid-liquid extraction (Moustapha et al., 2006), or anion-exchange controlled liquid-solid sorption from aqueous target solutions (Bidokhti et al., 2010; Shigeta et al., 1996; Zhang et al., 2001). If wet-chemical processing is considered, WO_3 is quite attractive as its recycling scheme may require fewer steps. Another attractive feature for using WO_3 is its lower melting point of 1473°C, which opens the potential for sintering targets to make them more structurally robust (and thus allow higher beam currents). Based on these considerations, both W metal and WO_3 target materials were evaluated in this investigation. The experimental approaches and results obtained relating to the characterization, suitability, and durability of pressed powder thick targets made from natural abundance W or WO_3 powders, and enriched ^{186}W powder, under deuteron bombardment are reported herein.

2. Materials and Methods

2.1. Cyclotron and target facility

The University of Washington Medical Cyclotron Facility's, variable energy, positive ion, multi-particle Scanditronix MC50 compact cyclotron was used in the irradiations. While the primary use for the cyclotron is treatment of cancer using Fast Neutron Therapy, beamlines to two target stations are used for the production of radionuclides. Radionuclide productions that use alpha particle irradiations occur on a target station installed on the 0° beamline to optimize production in those irradiations (Balkin et al., 2013; Stevenson et al., 2015). Irradiations with deuterons are conducted on an experimental target station installed at the terminal portion of a second beamline. On that beamline the extracted deuteron beam exits the cyclotron at 0°, is bent to the right 21° by a switching magnet, then another magnet, just upstream of an experimental target station, bends it an additional 48° to the right before reaching the target.

2.2. Target materials

Thick targets were prepared using powdered commercially available natural abundance W, as W metal or WO_3 (Alfa Aesar, Ward Hill, MA). In some experiments enriched (96.86%) ^{186}W metal (Isoflex USA, San Francisco, CA) was used. The isotopic W contaminants in the enriched material were certified to be 0.01% ^{180}W , 0.33% ^{182}W , 0.03% ^{183}W , and 2.77% ^{184}W . Commercially sourced WO_3 powder was used without alteration or after drying in an oven at 100°C for 24 hours. Thick targets were also prepared from natural abundance WO_3 obtained by in-house oxidation and chemical processing of powdered natural abundance W metal. WO_3 was prepared in-house from W metal in recognition of the fact that use of costly enriched ^{186}W target material will eventually require preparation of targets from material recovered from the processing waste stream (which contains WO_3). The conversion of W to WO_3 was achieved by dissolution of W metal powder in 30% H_2O_2 . The resulting solution was heated at 80°C for 30 minutes to decompose the peroxide prior to basification with an equal volume of 3M $(\text{NH}_4)_2\text{CO}_3$. The decomposition solution was allowed to cool to room temperature, followed by the addition of an excess of concentrated HCl to the reaction vessel to facilitate precipitation of WO_3 . The resulting mixture was allowed to equilibrate for 24 hours, then the liquid phase was decanted and the precipitate washed twice with 18 MΩ•cm deionized H_2O . Following the wash steps, the solid was isolated and dried in a VWR model 1320 drying oven (Radnor, PA) at 105°C for 48 hours. The recovered, hydrated, WO_3 was calcinated in a Lindberg/Blue M Mini-Mite Tube Furnace (Thermo-Fisher, Waltham, MA) at 800°C for 4 hours, allowed to cool to ambient temperature, and pulverized with a mortar and pestle to homogenize particle mesh size.

2.3. Preparation of W and WO₃ targets.

Deuteron beam full-stopping thicknesses for W or WO₃ targets were calculated using the SRIM software (Baum and Kulkarni, 2012), with published density values (Lide, 2006) for each target material, under the assumption that no water was present after drying. The methods used for preparing targets for irradiation are described below.

Electrophoretic deposition. Electrophoretic deposition (EPD) of W and WO₃ powders was evaluated on aluminum, copper, and tantalum foils. Briefly, strips of metal approximately 7.5 cm x 3 cm were connected via electrical lead to a Novex PowerEase 500 high voltage power supply (Life Technologies, Carlsbad, CA). To a 500 mL beaker was added 350-400 g of powdered W and solvent systems of either isopropyl alcohol or acetone with ~2% benzoic acid or zein – a prolamine protein found in corn – (by mass of W) or nitromethane with ~2% citric acid (by mass of W). EPD was conducted under high-voltage (350-500 V) with <1 mA of current for <15 minutes. After each deposition, the sample was dried at 100°C for 1 hour, followed by heat curing under Ar or a 2% H₂/N₂ gas mixture for 1 hour in a Carbolite MTF 12/38/400 tube furnace (Verder Scientific, Haan, Germany) at 500°C for Al foil, 900°C for Cu foil, or 1100°C for Ta foil.

A vertical deposition chamber was employed in some experiments. The chamber consisted of a threaded Teflon insert with an 11 mm diameter hole (see Figure S1, Supplemental Information). The aluminum base was constructed with a milled depression upon which the target support plate sat (this depression also assisted with alignment). The use of a metallic base allowed for electrical contact between the base and the target support. An o-ring groove in the Teflon made a seal with the target plate allowing for vertical introduction of a tungsten/nitromethane solution. Parts of the target backing that would not be exposed to the deuteron beam was covered with Bytac® PTFE surface coating with adhesive backing (Saint-Gobain Performance Plastics Corp., Valley Forge, PA). This procedure allowed the tungsten to deposit only on the area that would be irradiated, and provided an efficient recovery of any enriched tungsten that was not deposited. Electrophoretic deposition of W was obtained as described above.

Sintering. Attempts were made to sinter natural abundance W and WO₃ powders using two tube furnaces with different temperature ranges. In some sintering attempts, W or WO₃, as loose powders or pressed pellets (see below), were placed in a quartz boat then inserted into a quartz tube inside a Carbolite model MTF 12/38/250 tube furnace (Verder Scientific, Haan, Germany). Samples were introduced into the furnace at ambient temperature and were subsequently heated to 1100-1105°C under flowing N₂/H₂ or N₂ atmosphere and held at that temperature for 2 – 8 h. The furnace temperature was increased from ambient to the sintering temperature at 10 °C/min to reduce the thermal stress on the quartz tube. In attempts to sinter W metal, use of a high-temperature tube furnace (Carbolite model STF 16/180 single zone tube furnace) was also investigated. Pressed W metal pellets were placed in a tantalum boat (with cover) and then introduced into an alumina processing tube, which was subsequently heated to 1550°C under an Ar atmosphere and held at that temperature for 2 – 12 hours. Samples were introduced into the high-temperature furnace at ambient temperature and were heated to 1550°C by increasing the temperature at 5 °C/minute to minimize the thermal stress on the alumina tube. After the samples were heated for the predetermined time, the furnace and sealed work tube were allowed to cool to ambient temperature under N₂ or Ar before they were removed from the oven.

Uniaxial Pellet Pressing. Pressed targets were prepared by uniaxially pressing powdered W or WO₃ into 13 mm diameter pellets under 13.8 MPa of pressure using a Carver model C hydraulic laboratory press (Carver Inc., Wabash, IN). In most cases, the pellets were pressed directly into a machined aluminum target support (grade 6061 aluminum). However, in an effort to augment the robustness and overall durability of target pellets, two additional preparative techniques were evaluated. One technique was to press W powder between layers of powdered graphite (50 mg on the bottom and 100 mg on top) under 13.8 MPa pressure as described above. A second technique evaluated prepared WO₃ targets by pressing the powder separate from a machined aluminum target support using a 13mm KBR Pellet Die (International Crystal Laboratories, Garfield, NJ), followed by heating the resultant pellet in an attempt to sinter it, as described above. The thermally treated WO₃ pellets were placed into an aluminum target support for irradiation.

2.4. Target material characterization, composition analyses and target structural integrity

Samples of non-irradiated, natural abundance target materials (commercially available W metal, WO₃, as well as in-house produced WO₃, and graphite stabilized natural abundance W metal) were characterized by Fourier Transform Infrared (FTIR) spectroscopy using a Bruker Vertex 70 FTIR spectrometer with an Attenuated Total Reflectance (ATR) attachment

and a resolution of 4 cm^{-1} . Signal from a clean silicon wafer was used as background. Raman spectral comparisons of WO_3 were acquired on a home-built system using a Coherent Compass 532 nm laser with an output power of 5 mW focused onto the sample with a Mitutoyo 50x objective ($\text{NA} = 0.55$). Back-scattered photons were collected with the same objective and focused into an Acton SpectraPro 500i spectrograph with a Princeton Instruments liquid nitrogen-cooled silicon CCD camera. Fifty spectra with 100 ms acquisition times were averaged. X-ray Diffraction Spectroscopy (XRD) measurements were performed on a Bruker D8 Discover with GADDS XRD system using a Cu K_α X-ray source ($\lambda = 1.54\text{ \AA}$) and 300 second collection time.

Pressed targets were visually inspected for cracking and integrity. Non-irradiated pellets prepared by the methods described (uniaxial pressed non-sintered, sintered, and graphite encased) were evaluated using Scanning Electron Microscopy (SEM) for the purpose of assessing target material suitability and structural integrity. Target pellets prepared with and without sintering were imaged using an FEI Sirion scanning electron microscope at an accelerating voltage of 5kV in secondary electron imaging mode. Additionally, SEM was used to provide assessments of the graphite encasement as a method for pellet stabilization, as well as the completeness of the sintering process on WO_3 samples from each of the three heating durations.

2.5. Deuteron beam irradiations

Pressed, sintered, or graphite encased thick W or WO_3 targets (600-1100 mg) were irradiated under the deuteron beam conditions shown in Table 1. In the case of the targets structurally stabilized with graphite encasement, beam degradation by the top graphite layer was calculated by SRIM, and the incident deuteron energy adjusted to allow for comparison between target configurations. During bombardment, the aluminum target holder and target pellet were positioned 90 degrees to the incident deuteron beam, centered on target, and open to vacuum on the target material side. The target assembly was cooled using a water stream with a flow rate of 10 L/min from the side opposite the pressed W or WO_3 powders. Irradiations of pressed W powder began with a ramp of the current from approximately 1 μA to the desired intensity over a period of ~30 seconds, to allow for any outgassing from the target at the start of bombardment. This was accomplished without appreciable vacuum fluctuation. All W metal targets were irradiated for 10 minutes at 10 μA at each of 5 energies: 15 (15.05 ± 0.05), 17 (17.07 ± 0.06), 20 (20.03 ± 0.07), 22 (21.99 ± 0.08), and ~24 (23.85 ± 0.08) MeV. A more conservative approach, where the current was ramped from approximately 1-10 μA over a period of ~2 minutes, was used with pressed WO_3 powder targets as the possibility of violent outgassing was anticipated. WO_3 target pellets were irradiated for a total integrated current of 10 minutes at 10 μA with a nominal extracted deuteron energy of 17 (17.07 ± 0.06) MeV. Following irradiation, targets were either left to decay overnight, or removed approximately 1-hour post irradiation to allow any short-lived radionuclides to decay. Targets were weighed prior to and following irradiation to determine reduction in mass, if any. Targets were assayed using an EG&G Ortec model GEM-18180-P HPGe detector system (Ametek, Oak Ridge, TN) with model 659 High Voltage supply and model 672 Spectroscopy Amplifier and Maestro software (version 7; Ametek, Oak Ridge, TN) to assess the radionuclides produced. The HPGe detector was calibrated with sealed sources of ^{133}Ba , ^{137}Cs , and ^{60}Co at a 0° distance of 24 cm. All HPGe assays were given sufficient acquisition time to generate a minimum of 10,000 net counts in the 137 keV ^{186}Re peak with a typical deadtime value of <8%. Spectra were also evaluated for production of the 1.37 MeV ^{24}Na peak, which would occur if the aluminum target holder had been unintentionally irradiated.

2.6. Isolation of ^{186}Re from irradiated ^{186}W

The irradiated thick (~600-1100 mg) ^{186}W powder targets were dissolved in the presence of the aluminum support plate by slow addition of 30% H_2O_2 . Following dissolution, the solution was gently heated at $\sim 60^\circ\text{C}$ until H_2O_2 decomposition substantially halted (i.e. significant decrease in bubbling). An equal volume of 3 M $(\text{NH}_4)_2\text{CO}_3$ was added to the dissolved tungsten solution to yield a final concentration of 1.5 M $(\text{NH}_4)_2\text{CO}_3$. Aliquots of the dissolved target material were obtained for measuring ^{186}Re yield. Separation of the ^{186}Re from the ^{186}W target material was accomplished by elution on a column packed with Analig Tc-02 resin (typically ~300 mg), which was preconditioned with 1.5 M $(\text{NH}_4)_2\text{CO}_3$. The Analig column

was loaded with the dissolved target solution and subsequently washed with ~40-50 mL of 1 M $(\text{NH}_4)_2\text{CO}_3$ to remove the ^{186}W . Radiorhenium was then eluted with 3 mL of H_2O preheated to ~80 °C. Typical ^{186}Re isolation yields were in excess of 80%.

Slight modifications to the foregoing procedure were made for processing irradiated graphite-encased ^{186}W powder targets. In those isolations, the targets were dissolved in the presence of the aluminum support plate by slow addition of 30% H_2O_2 , and the reaction was allowed to proceed to quiescence (typically ~45 min). Reaction completeness was secondarily assessed by the presence of floating graphite flakes as opposed to sunken solid material indicative of undissolved W metal. Following dissolution, the solution was gently heated at ~90 °C until quiescence was again observed (typically 60 - 90 min). The reaction mixture was then basified as previously described to reach a final concentration of 1.5 M $(\text{NH}_4)_2\text{CO}_3$. Aliquots of the dissolved target material were used for measuring ^{186}Re yield. Separation of the ^{186}Re from the ^{186}W target material was accomplished as previously described. The addition of a small amount of spun glass wool on the column acted as a coarse filter to keep the fritted filter of the column clear of graphite debris. Isolated yields of ^{186}Re were in a range of 70-79%.

Aliquots of eluted ^{186}Re from both methods were assayed using a Capintec model CRC-55tR dose calibrator (Capintec Inc., Ramsey, NJ) to determine the overall elution efficiency. The radionuclidic purity of the isolated ^{186}Re was assessed via repeated gamma-ray spectroscopy measurements as previously described. Recovery and reduction of the oxidized ^{186}W target material from the waste stream was accomplished by processing the $(\text{NH}_4)_2\text{CO}_3$ column wash and flow-through solutions. The solutions were slowly acidified with a volume of concentrated HCl sufficient to precipitate a yellow/green solid (~130 mL), after which an additional 20 mL of concentrated HCl was added to ensure completeness of the reaction. The precipitate was vacuum filtered, washed with H_2O , and dried in air to provide $^{186}\text{WO}_3$ for recycling of target material. Development and characterization of this recycling method is ongoing.

3. Results

3.1. Target preparation by electrodeposition and sedimentation/annealing

Initial EPD studies, evaluating various solvent systems (i.e. acetone, isopropyl alcohol, and nitromethane), provided data that indicated nitromethane was the most promising solvent. EPD studies using that solvent demonstrated successful deposition of ~125 mg/cm² W metal and ~2 mg/cm² WO_3 onto aluminum backings within 15 min. The limited thickness obtained for WO_3 deposits made it unattractive for continued EPD studies. Deposition efficiencies with metallic W were >80%, which suggested that the approach was reasonable when considering using expensive enriched ^{186}W . Although preliminary EPD studies using W powder were successful, it was noticed that the adherence of the W to target backing materials was not optimal. Thus, optimization studies were conducted to explore deposition voltage, pH, solvent systems, electrode distance, target backing materials, post-annealing steps, etc. Examples of electrophoretic deposition of W and WO_3 on aluminum strips are shown in Figure 1. Natural abundance W metal was successfully deposited onto aluminum, copper and tantalum. Although deposits were reasonably adherent, they could be scraped off by physically rubbing the surface. Deposition in nitromethane containing citric acid (~2% by mass of W) as an additive appeared to give the most consistent depositions. Benzoic acid and zein (a prolamine protein found in corn) additives were also evaluated, as their use has been previously reported in the literature (Chen et al., 2013; Chen et al., 2014; Gutierrez et al., 1962; Keeler and Klach, 1959; Mizuguchi et al., 1983; Obata et al., 2003; Pearlstein et al., 1963; Seuss and Boccaccin, 2013).

While electrophoretic deposition onto metal strips was readily demonstrated, due to the cost of enriched ^{186}W it was deemed critically important to be able to recover the target material that was not deposited. Therefore, a vertical electrodeposition chamber was constructed (see Figure S1, Supplemental Information). A challenge encountered with the vertical EPD system was the removal of excess solvent following deposition. The excess solvent was removed by evaporation with heating, which resulted in bubbling and left pits in the tungsten. Alternatively, the solvent could be removed by evaporation, wherein the W or WO_3 was deposited by sedimentation. Using the sedimentation method, the tungsten/nitromethane suspension was loaded into the chamber and the nitromethane was allowed to evaporate without applying current. Although a deposition of several hundred milligrams of W metal (i.e., the thickness required to degrade the energy down to 0 MeV for $E_d =$

24 MeV) onto the metal target backing was achieved by both electrophoretic deposition and sedimentation (e.g. Figure 2), adherence of that quantity of W to the supporting plate was problematic. Attempts to anneal the W deposits under argon at temperatures of 500°C (on Al), 900°C (on Cu), and 1100°C (on Ta) showed no qualitative differences after heating. Similar results were noted for annealing of tungsten on either Al or Ta under 2% H₂/N₂ atmosphere. These results suggested that another approach to prepare thick W targets was required.

3.2. Sintering target materials

Sintering was evaluated as an approach to produce W or WO₃ targets that were more stable during irradiation. Sintering studies were conducted on natural abundance W metal and WO₃. Several experiments were conducted with the lower melting WO₃ (i.e. 1473°C). In two experiments, ~100 mg of natural abundance WO₃ was heated at 1100°C under an atmosphere of 2% H₂ / 98% N₂ in a tube furnace for 2 h. Those conditions resulted in the formation of a deep blue/violet colored solid, which upon analysis by energy-dispersive x-ray spectroscopy was determined to be a mixture of W oxides. In other experiments, masses of pressed pellets containing ^{nat}WO₃ (600-1100 mg) were heated at 1105°C under N₂ (without H₂). The experiments failed, as sintered WO₃ pellets were not obtained. Examination by SEM revealed that there was closer packing between grains of WO₃ powder as compared to the starting material, but the material did not have the characteristic “welded” or bonded appearance of a sintered substance.

Results from initial sintering experiments suggested that the sintering should be done at a higher temperature, so 600-1100 mg samples of ^{nat}WO₃ were heated at 1550°C in a tantalum boat under a N₂ atmosphere. Rather than annealing the powder to a solid mass, the WO₃ was completely reduced to W metal (section 3.2). Further attempts to create sintered pellets for use in the aluminum target backings included pressed thick targets (1000-1100 mg) of ^{nat}WO₃ that were heated under Ar at 1550°C were also unsuccessful. Since the WO₃ was converted to W metal, it was anticipated that there would be mass lost during the sintering procedure, but in this series of experiments the resulting pellets failed to achieve complete densification during the sintering process, resulting in unstable pellets with powdery centers. While the pressed WO₃ pellets had been converted to W metal, they were ultimately not useful since they could not be handled or irradiated without crumbling. Attempts to sinter W metal at 1550°C also failed, which was not surprising as 1550°C was too low for sintering the high melting point material (i.e. 3422 °C). Despite being unsuccessful in making usable pellets for irradiation, the thermal conversion of WO₃ provided an efficient method for recycling enriched ¹⁸⁶W.

3.3. Thick target preparation by uniaxial pressing

Thick targets were initially prepared by the uniaxial pressing of powdered W metal or WO₃ into an aluminum target backing that has a circumference of 25 mm with a 12 mm diameter depression that is 1.5 mm deep in the center (shown on right in top panel of Figure 3). Target pellets were formed by pressing the powder directly into the target support using a 13 mm anvil under various pressures (best results with 13.8 MPa) applied with a hydraulic laboratory press. While pressed W targets had reasonable stability when using beam amperages up to 10 µA, instability was noted when increasing to 20 µA. The instability was apparent as there was a loss of target material noted after irradiation, or the target fractured and part or all of it came loose from the target backing. There was concern that a non-uniform thickness was obtained when pressing due to the tolerances between the die and cavity in the aluminum backing. Changes made to the target backing design in an attempt to keep the pellet in the target backing if it came loose involved fabricating a target with a 10° angled in “dovetail” lip of 0.38 mm length. This approach was not successful, as it allowed pieces of the fractured targets to dislodge. Evaluation of attempts at sandblasting the target backing to provide better adherence during pellet compression actually resulted in decreased pellet stability. Targets were also prepared by pressing pellets separate from the aluminum backing using a commercially available enclosed 13 mm die (typically used for KBr pressing) under 13.8 MPa of pressure. While uniform target pellets were obtained, the process of removing them from the die resulted in unstable pellets. Pressing the powder in the die with commercially available paper ring supports (leaving an 11 mm pellet) was evaluated. While this procedure allowed the pellets to be easily removed, they were not stable. Due to the difficulties described, a two-piece aluminum target support in which the target cap had a smaller opening of 10 mm diameter, as opposed to the lower backing containing the 13 mm diameter well, was fabricated (Figure 3). This target holder gave satisfactory results, but stability of the pressed target was still an issue. To determine whether a pressed target might be unstable before irradiation, an initial test of the target design (pressed pellet in two-piece backing) was conducted by placing it on the beamline under high vacuum for 72 h without irradi-

ation to evaluate stability and loss of target material. A high vacuum storage vessel was also used to conduct the same assessment without having to occupy the target station on the experimental beamline.

Pressed natural abundance W metal and enriched ^{186}W targets were prepared with adequate stability to evaluate irradiations up to deuteron beam energies of 24 MeV. Although the W metal targets provided adequate stability for the short irradiations, there was concern about stability when conducting longer irradiations, and potential problems if higher beam amperages are used. Therefore, alternative target preparations that provided more stable targets were sought. An alternative that we believed might work was the use of pressed powdered graphite to serve as a malleable support to keep the W metal crystals together during and after irradiation. An initial study evaluated the stability of a W target that had 100 mg of powdered graphite pressed over 750 mg of W metal. This provided a very stable target configuration, but the W metal pellet was difficult to get out of the target backing without breaking up. A second study evaluated preparation of W target wherein 750 mg of W metal was pressed between two layers containing 100 mg each of powdered graphite. This configuration provided a pressed pellet that was readily removable from the aluminum target backing. Further studies demonstrated that encasement of pressed W targets with 100 mg graphite powder on top and 50 mg graphite on the back (next to aluminum) was a good configuration. While different in configuration, the use of graphite-W composites in irradiations on the U-120 cyclotron had been previously reported (Alekseev and Lazarev, 2006). Using the graphite-encased target composition, five natural abundance W metal and five enriched ^{186}W targets were also prepared.

WO_3 target pellets were prepared as described for W metal, except no graphite-encased targets were prepared. One of the more compelling reasons for using WO_3 as a target was that it might be easier to recycle the enriched ^{186}W . Thus, the natural abundance WO_3 powder used for target preparations was obtained either from a commercial source or by oxidizing natural abundance W metal to WO_3 . Visual comparison between the commercially available and chemically processed WO_3 target materials revealed appreciable differences in the color of samples. The commercially available WO_3 appearing dull, pale green, compared to the brighter yellow color of the in-house chemically processed powder (Figure S2, Supplemental Information). Analysis of the chemically processed WO_3 powder by FTIR spectroscopy indicated the initial (pre-calcined) product was tungstic acid, having strong $-\text{OH}$ group absorption bands at 1500 and 3300 cm^{-1} (Figure S3, line ii; Supplemental Information) and WO absorption at 600 cm^{-1} (Nakamoto, 1963). Removal of coordinated water, accomplished through calcination under ambient atmosphere at 800°C for 4 hours, produced a yellow powder, which despite the difference in color was shown to be comparable to the commercial sample by spectroscopic methods. Analysis of the calcined WO_3 product by FTIR confirmed the absence of the $-\text{OH}$ group absorption (Figure S3, line i; Supplemental Information) and Raman spectroscopy (Figure S4; Supplemental Information) supported the composition ascribed from the FTIR spectrum. Of particular interest are the presence of stretching (721 and 812 cm^{-1}) and bending (279 cm^{-1}) modes for W-O absent any detectable water modes. Previous reports (Daniel et al., 1987; Nishide and Mizukami, 1995; Nogueira et al., 2004; Ramis et al., 1990) describe the FTIR and Raman spectra of WO_3 and its hydrated form, tungstic acid, with varying degrees of water coordination. The FTIR spectrum reported here would suggest a formula of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ pre-calcination. Both FTIR and Raman show that after calcination there is no longer a detectable signal from coordinated water, indicating the presence of nearly pure WO_3 . Furthermore, comparison of the X-ray diffraction patterns obtained from both the calcined and commercially available WO_3 powders (Figure S5; Supplemental Information) indicates a virtually identical chemical composition with the structure of the calcined WO_3 product matching the reported literature values for a monoclinic crystal system (Filho et al., 2001; Lu et al., 2002).

3.4. Deuteron irradiation and isolation

A number of natural abundance and enriched uniaxially pressed W targets were irradiated with deuterons. No irradiations were conducted with the thick targets produced by electrophoretic deposition due to their instability. Thick, natural abundance, WO_3 target pellets prepared by uniaxial pressing either in an aluminum target backing or in a KBr press, were to be irradiated with 17 MeV deuterons ramping the beam current from 1 to 10 μA over ~2 min. However, during the first irradiation the maximal beam current was never reached as the target material was unstable upon contact with the deuteron beam, causing beamline vacuum fluctuations and allowing direct irradiation of the aluminum target body (as detected by production of ^{24}Na). Upon retrieval of the target support it was observed that the WO_3 had vaporized, discoloring the surface

of the well in the aluminum target support (Figure 6) and coating the walls of ~61 cm (24 inches) of the terminal portion of the beamline, which then required decontamination. We believe that these observations are the result of outgassing oxygen species that subsequently reacted with the aluminum target support. While these findings are in sharp contrast with the successful production and isolation as reported by both Fassbender et al. (Fassbender et al., 2013) and Shigeta et al. (Shigeta et al., 1996), we believe that these results are attributable to the target design necessitated by our current target station. Both previously successful studies reported utilizing an enclosed target with cooling in front and behind the target, whereas we are limited to rear side target cooling only with an open front target design. As no irradiated material was recovered, gamma-ray spectroscopy was only used to determine the extent of the activation of the aluminum target supports. To minimize further beamline contamination, work with WO_3 was ceased and all efforts were focused on irradiation of W metal targets.

Pressed W metal targets were irradiated for a period of 10 min using a 10 μA deuteron beam current at 15, 17, 20, 22 and 24 MeV, as described above (Table 1). Experience gained using natural abundance targets allowed development of methods to be used in target preparation for irradiation of enriched ^{186}W target materials and isolation of ^{186}Re . To determine the ^{186}Re production yields and isotopic ratios at the different beam energies, five pressed enriched ^{186}W targets were prepared. Following each irradiation, the target was dissolved and processed to isolate the ^{186}Re . The isolation procedure consisted of target material dissolution with 30% H_2O_2 , followed by heating to facilitate decomposition of any remaining H_2O_2 . The mixture was then brought to a basic pH with the addition of 3M $(\text{NH}_4)_2\text{CO}_3$, and passed over a ~300 mg column of Analig Tc-02 resin with a glass wool filter to remove any graphite and the column was eluted with 80 °C water. To assess production and isolation yields as well as radionuclidic byproducts, gamma-ray spectroscopy was performed on aliquots of the dissolved solution and extracted activity. Isolated radiochemical yields of between 70 and 79% were typical with decay-corrected saturated yields ranging from 1.47 ± 0.08 to 2.27 ± 0.12 GBq/ μA . Yields of the ^{183}Re and $^{184\text{g}}\text{Re}$ contaminants ranged between 0.045 ± 0.003 to 0.610 ± 0.042 % and 0.38 ± 0.02 to 4.43 ± 0.27 % respectively. The decay corrected radiochemical production results and yields of ^{183}Re and $^{184\text{g}}\text{Re}$ (relative to ^{186}Re) from those irradiations are provided in Table 2. This data is also presented graphically (Figure 7), with comparisons made to published yield data as obtained on the EXFOR database. It should be noted that several of the previously published yields were measured on natural abundance W (extrapolated here to ^{186}W) and/or were published based on calculations from stacked foil irradiations. In general, good agreement with the literature is observed. The reason for the anomalously low yield at 24 MeV in these studies is unknown, but might be explained by rhenium volatility either during bombardment or dissolution with 30% H_2O_2 .

Irradiations of graphite-encased natural abundance W and enriched ^{186}W targets were conducted using the same beam energy and amperage as used with W targets not encased in graphite (Table 1). The incident deuteron beam energy was adjusted for slight degradation of beam energy due to passing through the graphite layer, so that the production yields and abundances of other co-produced Re nuclides could be directly compared. The pressed graphite encased ^{186}W target produced identical percentages of the isotopic contaminants 183 and $^{184\text{g}}\text{Re}$ to targets pressed without the addition of graphite layers, as shown in Table 2. To evaluate their integrity after irradiation, the mass loss of each target was assessed. In each case the loss was <1%. As previously stated, the presence of the two layers of graphite necessitated modification of the isolation method to include a higher H_2O_2 decomposition temperature and increasing time for the isolation steps to allow each reaction to come to quiescence before proceeding to the next step. With these modifications in place, isolated radiochemical yields of targets produced with or without graphite enhancement were found to be within tolerable limits ($\pm 10\%$) of each other.

4. Discussion

The lack of availability of high specific activity ^{186}Re has hampered the development of radiopharmaceuticals using this theranostic radionuclide. For example, our research group is interested in using ^{186}Re in pretargeted radioimmunotherapy studies (Green et al., 2014; Orozco et al., 2014; Pagel et al., 2009a; Pagel et al., 2009b), but lack of availability has precluded us from conducting those studies. Prior literature reports were suggestive that deuteron irradiations of enriched tungsten targets could potentially provide a method by which high specific activity ^{186}Re could be obtained, but scale-up to a production level had not been previously demonstrated. The significantly higher production rate when using deuteron versus proton irradiations made that approach attractive for use in our cyclotron facility, as the facility has deuteron beam capability. Thus, we conducted this investigation to evaluate production of high specific activity ^{186}Re using deuteron irradiation of enriched

^{186}W thick targets. As part of the investigation, methods were studied for preparing robust thick targets that would withstand the higher beam amperages required for production runs, and would be compatible with high yield ^{186}Re isolation methods as well as ^{186}W recycling.

Three strategies were considered for preparation of thick W or WO_3 powder targets, including electrophoretic deposition (EPD), hydraulically pressed pellets (with or without metal backing) and augmentation of pressed target pellets using sintering and encasement with graphite. Although electroplating has been used for many other solid target systems (e.g. ^{64}Ni plating for ^{64}Cu production (McCarthy et al., 1997; Obata et al., 2003)), electrophoretic deposition of tungsten was not considered straightforward, particularly when thick deposits are desired. However, EPD techniques for making thick deposits of tungsten had been previously reported (Gutierrez et al., 1962; Keeler and Klach, 1959; Mizuguchi et al., 1983; Pearlstein et al., 1963), so studies were conducted in this investigation to evaluate whether that approach could be used to prepare suitable targets. Enriched ^{186}W and $^{186}\text{WO}_3$ powders are readily available from commercial sources, but less costly natural abundance W powders (both metal and WO_3) were used in most experiments to minimize the cost of the studies. In addition to the purchased WO_3 powder, WO_3 was also prepared in-house by oxidation of W to evaluate the potential for recycling enriched WO_3 from the processing of prior irradiated targets. The studies began with attempts to deposit W and WO_3 on metal surfaces. The amount of WO_3 that could be electrophoretically deposited was too low to be useful for preparing thick targets. While W metal targets could be prepared by EPD, under the conditions studied the deposited W was not adequately adherent to the aluminum backing for irradiation. An alternate method for depositing W or WO_3 on metals was to use sedimentation in a vertical chamber. It was understood that this method would not provide robust targets by itself, but it was thought that suitable targets might be obtained if an annealing process could be done on the deposited W. It appeared that there was an increase in structural stability of the final pellets, but it was believed that the targets would not hold up under the conditions of the high vacuum and increasing beam amperage.

Target preparation by uniaxial hydraulic compression of dry W or WO_3 powders was generally found to be a reliable technique, with successful pressing of pellets into the aluminum target supports. However, pressed pellets were found to show signs of instability (hairline cracks on the surface of the pellet) 24-hours post compression, in some cases resulting in inverted material falling out of the target support. Additionally, if the surface of a cracked pellet was touched or wiped, a removable residue was readily apparent. Pressed targets were therefore irradiated within 3 hours of target preparation. Alternative target preparation approaches using the uniaxial pressing procedure were explored for preparing W and WO_3 targets. In one experiment, a WO_3 pellet was pressed separate from the aluminum backing, then heated in an attempt to sinter the pellet to provide higher stability. The sintering process forms a solid mass of material by heat and/or pressure without melting it to the point of liquefaction (WO_3 $t_{\text{melt}} = 1473^\circ\text{C}$), and is a common manufacturing technique used with metals, ceramics, plastics, and other materials (Kingery et al., 1976). During the sintering process atoms in the material diffuse across boundaries, fusing particles together and creating one solid piece. Because the sintering temperature does not have to reach the melting point of the material (typically 75-80 % of t_{melt}), sintering is often chosen as a shaping process for materials with very high melting points (Kingery et al., 1976). Attempts to sinter a WO_3 pellet at 1105°C (75% of t_{melt}) yielded surprising results. In contrast to the characteristic annealed appearance of a sintered material, grains of the WO_3 sample appeared more densely packed, but not fused to one another irrespective of the heating time used. Although the process increased the packing efficiency of individual WO_3 grains, SEM micrographs of the 12-hour, 1105°C sintered target showed no appreciable fusing of grains, as noted by the individual grain boundaries (Figure 4). Furthermore, the sintered target pellets were found to be quite brittle and prone to crumble, another indication that sintering had not occurred.

Uniaxial pressing of full-thickness W metal powder pellets was also found to be problematic for similar reasons as those described for WO_3 . The initial pressed pellet (Figure 5a) appeared to be stable, but its stability diminished in a matter of hours, particularly when handling the target. In some studies, this instability resulted in loss of W target material in the target station. SEM micrographs revealed that the W in the pressed target had a “loosely packed” and highly crystalline structure (Figure 5b), which appeared to result from the material relaxing the hydraulic compression after a relatively short period of time. The continuing concern for structural integrity of ^{186}W pressed targets led to consideration of ways to stabilize the pellets. Binder materials, such as high boiling organic materials, were considered, but there were concerns about degradation of the binders with outgassing. There was also a concern about converting the enriched W to WC, which might result in difficulties in recycling of enriched W. Fortunately, uniaxial pressing of W between two layers of graphite (similar to a sandwich) was found to greatly enhance the stability of the pressed target. (Figure 5c). Indeed, targets constructed in this manner

were found to be stable under high-vacuum for several days without detectable loss of target mass. An explanation for how encasement of W by graphite layers enhanced stability was obtained from SEM micrographs, as they showed that the powdered graphite conforms to the cavities between the W metal crystals (Figure 5d) which holds the W pellet together. Importantly, this encasement of W with graphite does not appear to be detrimental in the overall isolation process, as it was demonstrated that very similar processing techniques to those used without the presence of graphite gave reasonably high ^{186}Re isolation yields (79%) and acceptable recovery of $^{186}\text{WO}_3$ (80%).

Obtaining stable targets by pressing the W metal proved to be difficult due to the refractory nature of that material. If one could obtain enriched W metal foils target stability would not be an issue, however, the cost for making enriched metal foils makes that option untenable. Sintering of W metal targets is also not possible at our facility, as the available furnaces do not begin to approach its melting point of 3422°C. Recently, Lapi et al have described production and irradiation of enriched tungsten carbide (^{186}WC) targets for production of high specific activity ^{186}Re (Richards et al., 2015). While this approach is attractive for target fabrication, the effort that is required to conduct the multiple steps and the time involved in the isolation process does not appear to have any advantages to the use of graphite-encased ^{186}W metal targets. This fact supports continued studies with the graphite-enhanced ^{186}W targets for scale-up production of high specific activity ^{186}Re .

5. Summary and conclusions

This investigation was undertaken as prior literature was suggestive that deuteron irradiations of enriched W or WO_3 targets could provide adequate quantities of ^{186}Re for preclinical studies and follow-up clinical studies. In the investigation it was found that preparing thick W metal targets for deuteron irradiation was very challenging due to the refractory nature of tungsten. The fact that we were not successful in preparing a WO_3 thick target that withstood deuteron irradiation is disappointing. However, ^{186}W thick targets were prepared and irradiated with deuterons at various energies to determine production rates. In reality, the pressed W targets were only marginally acceptable, so a method of stabilizing the targets by pressing the W metal between two layers of graphite powder was developed. This graphite encased target approach greatly increased the stability of the W metal targets. Indeed, it appears that uniaxial pressing of W metal placed between two layers of graphite is a viable target material for ^{186}Re production in our facility (and elsewhere). Options for improved target stability, such as using high purity aluminum foil to cover W or $^{186}\text{WO}_3$, may provide another approach for production of high specific activity ^{186}Re . However, that production route would produce large quantities of ^{24}Na , making it difficult to handle in our facility. The results obtained in this investigation indicate that bombardment of graphite-encased W metal targets with 17 MeV deuterons at a current of 10 μA provides a reasonable balance of target material required and radionuclidic purity (^{186}W vs. coproduced ^{183}W & ^{184g}W) while providing reasonable ^{186}Re production yields under saturation conditions (1.81 ± 0.09 GBq/ μA). Based on these results, additional studies are being undertaken with deuteron irradiation of graphite-encased ^{186}W targets to demonstrate GBq (mCi)-scale production of ^{186}Re and recycling of the ^{186}W target material.

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Figures with Captions

Fig. 1. Photographs of W metal and WO₃ deposited on aluminum foil by EPD using a nitromethane solvent system. (a) Direct deposition of W metal, (b) deposition of W metal in a specified/controlled location through masking of conductive surface with Bytac® PTFE adhesive, and (c) deposition of natural abundance WO₃. U.S. pennies are shown to provide relative measures of aluminum strip size.

Fig. 2. Photograph of an aluminum target backing prior to electrophoretic deposition (left) and after deposition (right) of natural abundance W metal.

Fig. 3. [Top panel] Photographs of unassembled aluminum target support showing (on left and middle) both sides of target cap and (on right) target backing, [Bottom panel] Assembled target shown at two angles. Measurements of target support are: upper and lower circumference = 78.5 mm; upper target cap hole diameter = 10 mm on target center; lower target support well diameter = 12 mm on target center.

Fig. 4. Scanning electron micrograph of WO₃ target material heated at 1105°C for 12 hours. (scale bar = 2 μ m)

Fig. 5. (a) Photograph of powdered W metal (dark center) uniaxially pressed into an aluminum target support. (b) Scanning electron micrograph of the pressed powdered W metal structure (scale bar = 10 μm). (c) Photograph of pressed W target (dark center) which consisted of two layers of graphite encasing a layer of powdered W metal. (d) Scanning electron micrograph of the graphite layer covering the top of a pressed W layer. The graphite layer has been lifted to expose the powdered W metal (scale bar = 50 μm). Note that the pressed powder graphite can be pulled back in the form of a sheet that covers crystals of W metal, which makes it possible to separate the graphite and metal during isolation of ^{186}Re .

Fig. 6. Photographs of: (left) a 13 mm uniaxially pressed WO_3 target pellet in an aluminum backing for irradiation. The WO_3 target had been heated at 1105°C for 3 hours (to sinter), then was placed in the target holder; (right) Remnants of the WO_3 target in its aluminum holder after irradiation with 15 MeV deuterons at 10 μA for 10 min. The thin ring of material remaining in the target holder cavity was caused by the overlap of the donut shaped upper portion of our target body assembly (see Figure 3).

Fig. 7. (left) Ratio of ^{183}Re and ^{184g}Re relative to ^{186}Re (decay corrected to EOB), and (right) measured saturated yields with comparison to published literature (scaling $^{\text{nat}}\text{W}$ data to enriched ^{186}W).

Tables

Table 1: Target materials, configurations and conditions used in deuteron irradiations.

Target Material	Preparation Method	Deuteron Beam Energy*	# Irradiations
^{nat} W _{metal}	pressed pellet	15, 17, 20, 22 & 24 MeV	10**
^{nat} W _{metal}	graphite encased	15, 17, 20, 22 & 24 MeV	5
^{nat} WO ₃	pressed pellet	17 MeV	1***
^{nat} WO ₃	sintered pellet	17 MeV	1***
¹⁸⁶ W	pressed pellet	15, 17, 20, 22 & 24 MeV	5
¹⁸⁶ W	graphite encased	15, 17, 20, 22 & 24 MeV	5

*Beam current of 10 μ A was used in all listed irradiations

** Two irradiation were conducted at each beam energy

***Evaluation resulted in unsuccessful irradiation with beamline contamination

Table 2: Production yields of ^{186g}Re at saturation and relative abundances of coproduced ¹⁸³Re and ^{184g}Re from deuteron irradiation of enriched ¹⁸⁶W metal powder.

E _d (MeV)	^{186g} Re Y _{sat} (GBq/ μ A)	¹⁸³ Re/ ^{186g} Re (%)	^{184g} Re/ ^{186g} Re (%)
15	1.47 $\pm$ 0.08	0.045 $\pm$ 0.003	0.38 $\pm$ 0.02
17	1.81 $\pm$ 0.09	0.131 $\pm$ 0.007	0.39 $\pm$ 0.02
17**	1.81 $\pm$ 0.09	0.131 $\pm$ 0.007	0.39 $\pm$ 0.02
20	1.96 $\pm$ 0.11	0.311 $\pm$ 0.021	0.45 $\pm$ 0.03
22	2.27 $\pm$ 0.12	0.448 $\pm$ 0.023	1.41 $\pm$ 0.07
24	1.61 $\pm$ 0.07	0.610 $\pm$ 0.042	4.43 $\pm$ 0.27

*Values are decay corrected

**Pressed W target was encased in graphite