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# Manufacture of Tl targets by electrodeposition for the study of excitation functions of $^{203}\text{Pb}$

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**Abstract.** Natural Tl targets were manufactured by electrochemical deposition on a foil gold backing. The electrochemical parameters were defined after several experiments and reverse pulse potential was chosen to avoid the formation of filaments and dendrites. Once these parameters were established, enriched  $^{205}\text{Tl}$  targets were manufactured on a gold foil backing to be used to measure the cross sections for  $^{203}\text{Pb}$  production by deuteron induced reactions. The production yield was calculated from our excitation functions and was found to be 54 MBq/ $\mu\text{Ah}$  in the energy interval 32.5 MeV – 30 MeV.

## 1 Introduction

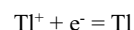
$^{203}\text{Pb}$  radiopharmaceuticals are good candidates for SPECT imaging [1] as  $^{203}\text{Pb}$  emits a strong 279 keV gamma line and has a half-life of 51.9 h [2]. This interesting radionuclide forms the diagnostic part of the  $^{203}\text{Pb}/^{212}\text{Pb}$  theranostic pair, whereas  $^{212}\text{Pb}$  (10.65 h) [3, 4, 5] has been suggested for targeted alpha-therapy as it emits two  $\beta^-$  particles and one  $\alpha$  particle during its decay chain. The production of  $^{212}\text{Pb}$  is well known; it is eluted from a  $^{228}\text{Th}$  generator, while  $^{203}\text{Pb}$  can be produced by light charged particle (proton and deuteron) bombardment of natural thallium or enriched  $^{203}\text{Tl}$  or  $^{205}\text{Tl}$ .  $^{201}\text{Tl}$  radiopharmaceuticals [6] [7] are widely used and  $^{201}\text{Tl}$  is produced via a Pb precursor isotope from enriched  $^{203}\text{Tl}$  with proton beam. The industrial fabrication of  $^{203}\text{Tl}$  targets is achieved by electrochemical deposition using the method of bipolar chopped sawtooth form [6, 7]. This method requires a specific potentiostat/galvanostat, which is not always available in all industries or laboratories. A new method has been developed in this work based on electrodeposition. It has been used successfully to prepare thin targets to study the production of  $^{203}\text{Pb}$  by deuteron irradiation of enriched  $^{205}\text{Tl}$  as well as a thick target for large scale production. The stacked foil technique [10] was used to study the excitation functions of deuteron induced reactions on enriched  $^{205}\text{Tl}$  targets. The present results are compared with Adam Rebeles et al. (2012) who used natural thallium [11] and Blue et al. (1978) who used enriched  $^{205}\text{Tl}$  [12] in the energy range between 21 MeV and 34 MeV, and with the values

extracted from the TENDL-2021 nuclear data library [8].

## 2 Materials and Methods

Thin deposits of natural Tl were obtained by electroplating on a high-quality gold foil (15  $\mu\text{m}$  thick from Goodfellow, 99.90%). The plating solution was prepared with extreme caution due to the high toxicity of Tl. Beaker A, containing 1g  $\text{Tl}_2\text{O}_3$ , was filled with 0.5 mol/L EDTA, 0.4 mol/L NaOH, and 300  $\mu\text{L}$  BRIJ-35 20%, then ultra-pure water was added to 33.1 mL. Beaker A was covered with Parafilm and the solution was stirred with a magnetic rod at 300 rpm. Beaker B was filled with 1.9 mL hydrazine hydrate 35%. The solution of beaker B was transferred through capillaries with a peristaltic pump at a flow rate of 0.5 mL/min to the solution of beaker A. The foam layer formed on top of the solution disappeared after 5 min.

The solution was adjusted to pH 8 by adding NaOH or  $\text{H}_2\text{SO}_4$  as needed. This pH value was chosen because the Tl(I) and Tl(III) complexes with EDTA are stable at pH 8 [13], thus avoiding the precipitation of Tl(I) and Tl(III) hydroxide in the basic solution [14]. The electrodeposition occurred via the electrochemical reaction



with a redox potential of -0.336 V/NHE [15]. Other states of thallium exist in the solution, such as Tl(III) that forms during electrodeposition. Tl(III) can be produced by the oxidation of  $\text{Tl}^+$  on the auxiliary electrode to form thallium hydroxide or thallium oxide because of its redox potential of 1.252 V/NHE [15]. To

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avoid the formation of thallium oxide, hydrazine was used as a strong reducing anodic depolarizer. All chemical products mentioned were purchased from Sigma Aldrich.

The deposition was carried out in a homemade Teflon cylinder cell containing 35 mL of the electrolyte solution. A 20 mm diameter hole was placed on the side of the cylinder for the working electrode resulting in a  $^{205}\text{Tl}$  deposit of  $3.14\text{ cm}^2$ . A sealing film and a stainless-steel plate were used to ensure a leak tight cell and good electrical connection. The working electrode was a  $2.5\text{ cm} \times 2.5\text{ cm} \times 15\mu\text{m}$  gold foil. The auxiliary electrode was made from a 1 mm diameter platinum rod. A reference electrode Ag/AgCl/sat KCl was also used during the process. The distance between the working electrode and the auxiliary electrode was set at  $1.0 \pm 0.1\text{ cm}$ .

A PGZ 401 potentiostat/galvanostat was used to study the electrochemical behaviour at the interface between the solution and the substrate by voltammetry experiment, and to obtain different deposits by chronoamperometry according to voltammetric results following two different methods: one using direct potential and the other by reverse pulsing potential. The scanning potential was from 0 V/NHE to -1.4 V/NHE for three cycles. The scanning speed was 0.05 V/s and the duration of chronoamperometry was set to 1h. For all experiments, the solution was stirred at 750 rpm using a homemade Teflon propeller rod.

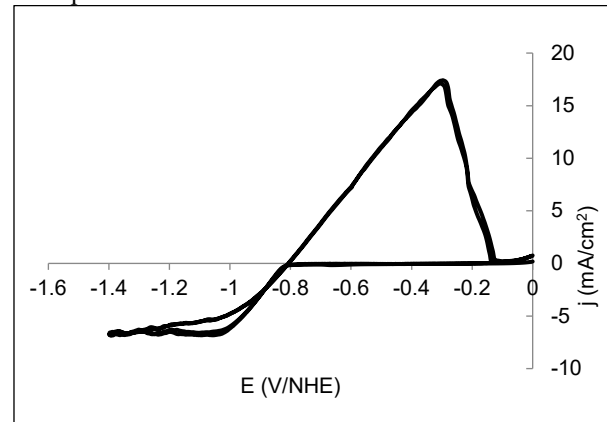
The surface morphology of the deposits was analyzed by JEOL JSM 7100F scanning electron microscope (SEM). Energy-dispersive X-ray spectroscopy (EDX) coupled to the SEM was also used to investigate the chemical composition of the surfaces. The stacked-foil technique [10] was used to perform production cross section measurements of deuteron induced nuclear reaction on enriched  $^{205}\text{Tl}$  (Trace Science International). The target deposits were manufactured by electrodeposition as previously described. Experiments were conducted at GIP ARRONAX [16] in Saint-Herblain - France, in the energy range from 21 MeV to 34 MeV. The measured production cross sections were compared with the experimental data available in the literature (e.g., on the database EXFOR [2]) and from TENDL-2021 [17].

### 3 Results and Discussions

#### 3.1 Voltammetry experiments

Figure 1 shows the voltammetry curves of  $\text{Tl}^+$  in the solution at pH 8. The behaviour of the curves remained unchanged for three cycles. Two peaks occurred, one at the reduction of  $\text{Tl}^+$  to Tl and one at the oxidation of Tl to  $\text{Tl}^+$ , at the potential of -1.0 V/NHE and -0.3 V/NHE, respectively. At -0.65 V/NHE, a small peak corresponds to the reduction of oxygen [18], which is inevitable. The curves drop at -0.8 V/NHE, which corresponds to the beginning of the reduction of  $\text{Tl}^+$  to a Tl deposit. At -1.0 V/NHE, the value of current density is at a maximum, -

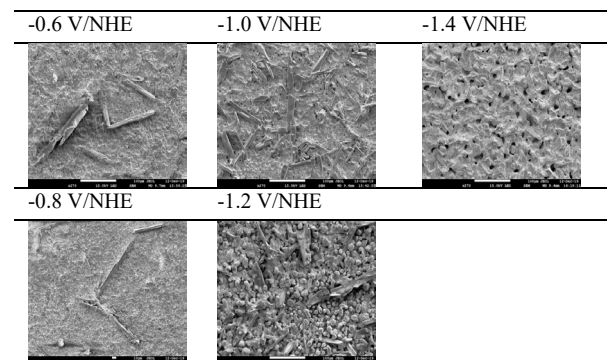
$6.8\text{ mA/cm}^2$  and below -1.2 V/NHE, the curves are disturbed because of the reduction of water. At return to -0.8 V/NHE, the curves rise until -0.3 V/NHE, which corresponds to the dissolution of the Tl deposit. The maximum value of current density is  $17.3\text{ mA/cm}^2$  and it drops to 0 at -0.12 V/NHE.



**Fig. 1.** Voltammetry curves of  $\text{Tl}^+$  in the solution containing 0.05 M  $\text{Tl}_2\text{O}_3$ , 0.5 M EDTA, 1.9 mL hydrazine, and 300  $\mu\text{L}$  BRIJ-35. The pH was adjusted to 8. Sweep from 0 V/NHE to -1.4 V/NHE for 3 cycles with a scanning speed of 0.05 V/s.

#### 3.2 Electrodeposition experiments: Direct potential

Five values of potential were applied: -0.6 V/NHE, -0.8 V/NHE, -1.0 V/NHE, -1.2 V/NHE, and -1.4 V/NHE. The deposits were characterized by SEM with the magnification x270, except for -0.8 V/NHE at x300 (Figure 2).



**Fig. 2.** Microscopic images of surface morphology of Tl deposits under different applied potentials: -0.6 V/NHE, -0.8 V/NHE, -1.0 V/NHE, -1.2 V/NHE, and 1.4 N/NHE.

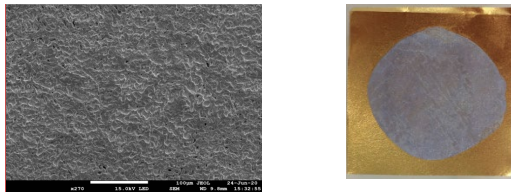
For each condition in Figure 2, the formations of filaments are clearly visible on the surface of deposits for the potentials from -0.6 V/NHE to -1.2 V/NHE. At -1.4 V/NHE, vacuoles are present on the surface structure, which means that evolution of hydrogen gas bubbles occurred due to reduction of water. Furthermore, the surfaces of the deposits were porous, with the notable formation of dendrites. These defects make the Tl deposit fragile and prone to failure during irradiation. These defects have also been described by van den Bossche et al. [8].

### 3.3 Electrodeposition experiments: Reverse pulse potential

To avoid the formation of these defects, the reverse pulse current with a bipolar chopped sawtooth form mode was used to obtain a smooth and dense Tl deposit, as suggested for the electrodeposition of Tl for the production of  $^{201}\text{Pb}$  from  $^{203}\text{Tl}$  [9]. In our case, this involved replacing the current applied approach by the potential approach with a bipolar chopped sawtooth form. Van den Bossche et al. [8] had proposed working with a signal frequency of 100 Hz, a chopper frequency of 1000 Hz, and a chopper duty cycle of 60%. Our potentiostat/galvanostat did not allow application of high frequency, so 10 Hz was chosen. Furthermore, the pulse was accurate with this frequency using our potentiostat/galvanostat. After several experiments, we established a suitable potential to reduce  $\text{Tl}^+$ , while avoiding the formation of filaments and dendrites. The electrochemical parameters are summarized in Table 1, along with two pictures: morphology under SEM at x270 magnification, and Tl deposit on gold backing.

**Table 1.** Electrochemical parameters to obtain a smooth and dense Tl deposit

Reduction potential	Oxidation potential	Reduction time	Oxidation time
-1.10 V/NHE	-0.730 V/NHE	60 ms	40 ms



**Fig. 3.** Microscopic image of surface morphology (left image) and photograph of a Tl on gold backing (right image). The Tl deposit is obtained by applying a reverse pulse potential (-1.10 V/NHE for 60 ms and -0.73 V/NHE for 40 ms).

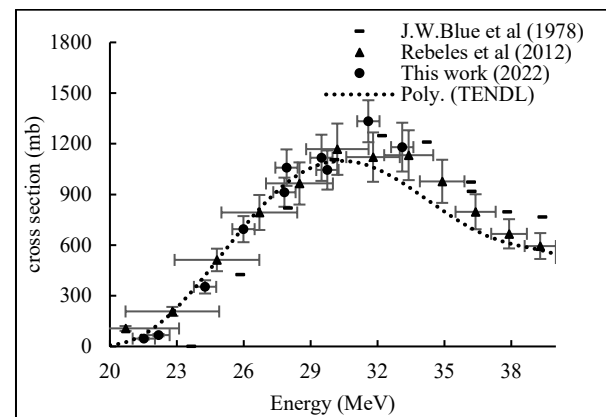
Figure 3 shows a smooth and dense Tl deposit free from filaments and dendrites. This deposit adheres strongly to the gold backing. The electrochemical parameters given in Table 1 were used to manufacture targets for measuring the excitation functions induced by deuterons on  $^{205}\text{Tl}$  to produce  $^{203}\text{Pb}$ .

### 3.4 Excitation functions of $^{205}\text{Tl}(d,4n)^{203\text{m}1+\text{m}2+\text{g}}\text{Pb}$

Five irradiation runs were performed at the ARRONAX facility in the energy range 21–34 MeV with deuteron beams, using the stacked-foil method. Each irradiation involved two targets of  $^{205}\text{Tl}$  deposits. The  $^{205}\text{Tl}$  were manufactured by electrodeposition within 1h, to obtain a deposit thickness in the range 10  $\mu\text{m}$ –15  $\mu\text{m}$ .

Figure 4 reports the  $^{205}\text{Tl}(d,4n)^{203\text{m}1+\text{m}2+\text{g}}\text{Pb}$  cumulative cross sections measured in this work in the energy range 21 MeV–34 MeV. The measured cross sections with the estimated total errors for this reaction at a certain energy are given in Table 2. Two existing studies in the literature are available: Blue et al. (1978) [12] and Adam Rebeles et al. (2012) [11]. The values of uncertainty from Blue et al. (1978) are not reported, and their values of cross section seem to be shifted in energy

by a few MeV, leading to an underestimation below 28 MeV and an overestimation above 34 MeV. These values agree with the present work between 28 MeV–34 MeV. Despite the fact that in Adam Rebeles et al. (2012) natural thallium was used, the production of  $^{203\text{m}1+\text{m}2+\text{g}}\text{Pb}$  above the energy of 23 MeV is mostly due to the nuclear reaction induced on  $^{205}\text{Tl}$  (natural abundance 70.48%). The values of cross section from Adam Rebeles et al. (2012) were rescaled to a 100% enriched  $^{205}\text{Tl}$  material and are in good agreement with our data. The values available in TENDL-2021 [1] (dotted curve in Figure 4) agree well with our data for the energy below 30 MeV. At higher energy, these values are lower than our data and those reported by other authors.



**Fig. 4.** Cross sections of the  $^{205}\text{Tl}(d,4n)^{203\text{m}1+\text{m}2+\text{g}}\text{Pb}$  nuclear reaction

**Table 2.**  $^{203}\text{Pb}$  measured cumulative cross sections of deuteron induced-reactions on enriched  $^{205}\text{Tl}$  (enrichment of 99.75%).

$E_d$ (MeV)	$^{203\text{m}1+\text{m}2+\text{g}}\text{Pb}$ (mb)
$21.5 \pm 0.5$	$46.5 \pm 5.2$
$22.2 \pm 0.5$	$67.0 \pm 6.9$
$24.3 \pm 0.4$	$352.6 \pm 39.1$
$26.0 \pm 0.3$	$694.4 \pm 77.2$
$27.8 \pm 0.4$	$913.1 \pm 86.2$
$27.9 \pm 0.4$	$1058.7 \pm 107.9$
$29.5 \pm 0.3$	$1116.8 \pm 136.8$
$29.8 \pm 0.3$	$1044.5 \pm 115.8$
$31.6 \pm 0.3$	$1333.3 \pm 124.3$
$33.1 \pm 0.3$	$1180.0 \pm 144.5$

## 4 Conclusion

In this work, we determined optimized electrodeposition parameters to obtain a dense and smooth Tl deposit. Good quality deposits were obtained by the application of reverse pulse potential, which suppressed filament and dendrite formation. The same parameters were used to manufacture enriched  $^{205}\text{Tl}$  targets for cross section measurements of  $^{203\text{m}1+\text{m}2+\text{g}}\text{Pb}$  through deuteron induced reaction in the energy range from 21 MeV to 33 MeV. Our data are in agreement with those reported by Adam Rebeles et al. (2012; within experimental errors), if scaling to 100% isotopic abundance is taken into account.

In general, the data available in the TENDL-2021 database show acceptable agreement with our experimental results.

Using our cross section data, we can estimate the  $^{203}\text{Pb}$  production yield in the energy range from 32.5 MeV to 30 MeV to be 54 MBq/ $\mu\text{A}/\text{h}$ . This energy range corresponds to a thallium thickness of 42  $\mu\text{m}$ .

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